Corrosion behavior of NiTi alloy in fetal bovine serum

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The corrosion behavior of NiTi alloy in fetal bovine serum (FBS) at 37 °C is investigated using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma mass spectrometry (ICP-MS). The presence of FBS moves the OCP to the negative direction and makes the oxide film thinner and more porous than that in phosphate buffer saline (PBS, pH = 7.4). The impedance of the oxide film formed in FBS is smaller than that in PBS, but the total interface impedance is bigger in FBS because of the formation of a surface bio-film. Pits form on the NiTi alloy after immersion in FBS for 200 h but they are not observed on the sample immersed in PBS. XPS shows that the composition of the oxide film formed in FBS is similar to that formed in PBS and it is composed of mainly Ti oxides with a small amount of Ti hydroxide. Hydrated Ti is observed on the outermost surface of the NiTi alloy. The thickness of the oxide film on the NiTi alloy immersed in PBS is 17 ± 3.0 nm and that on the sample immersed in FBS is 10 ± 3.2 nm. The results are consistent with those obtained by EIS. The presence of FBS can accelerate leaching of Ni ions and the mechanism is investigated and discussed.

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1. Introduction
Nitinol, a nearly equiatomic nickel–titanium alloy discovered in 1962 has been studied extensively for biomedical applications because of its unique shape memory effect, super-elasticity, as well as good biocompatibility [1–3]. However, human body fluids constitute a complicated electrochemical system and after implantation into the human body, corrosion of NiTi alloy occurs spontaneously to lower the free energy of the system. The corrosion behavior of NiTi alloy is spontaneous to lower the free energy of the system. The corrosion of NiTi alloy in human body fluids, but human body fluids are a complicated electrochemical system which contains not only inorganic species but also organic giant molecules such as serum proteins. Williams and co-workers [8] studied the corrosion behavior of Ti–6Al–4V, Ti–6Al–7Nb, and Ti–13Nb–13Zr in protein solutions and found the presence of albumin could improve their corrosion resistance. They suggested that a metal/protein/hydroxide complex could form on the surface thereby inhibiting the dissolution of metals. Fujimoto and co-workers [9] used different electrolytes to study the corrosion behavior of type 304 and 316L stainless steels and found that the fetal bovine serum (FBS) could decrease their corrosion resistance. They ascribed it to the presence of proteins which could increase the activity of the anodic process and decrease it in the cathodic process. Contu et al. [10] used electrochemical impedance spectroscopy (EIS) to investigate the electrochemical characteristics of commercial pure titanium (CP-Ti), Ti–6Al–4V, Ti–6Al–7Nb and Co–Cr–Mo alloys in FBS. They proposed that the compact adsorbed protein layer on the implant surface could act as a barrier to hinder charge transfer thus increasing the corrosion resistance. Nonetheless, up to now, not much work has been carried out to evaluate the influence of organic species such as proteins on the corrosion behavior of NiTi alloy, although this topic is very important to clinical applications.

In most studies involving industrial parts, the main concern is the corrosion resistance of the materials itself and the impact of corrosion products to the environment is usually negligible [11]. However, for biomedical implants, both of them are important equally. In the corrosion process of NiTi alloy in human body, the corrosion products such as Ni ions leach out from the bulk materials into surrounding tissues. Experiments based on the gene expression profiles demonstrate that Ni ions can suppress cell metabolism, differentiation, proliferation and induce cell apoptosis through changing the expression level of related genes [12]. It has also been reported that nickel ions can combine with biomolecules...
thereby acting as a possible source of allergy and toxicity [13]. Many researchers have measured the amounts of Ni ions leached from NiTi substrate after different immersion time in SBF [14–16], but data in real physiological environment such as FBS are still lacking.

In this work, we aim at studying the influence of FBS on the corrosion behavior of NiTi alloy at 37 °C using electrochemical methods. X-ray photoelectron spectroscopy (XPS) is used to determine the structure and thickness of the surface oxides. Scanning electron microscopy (SEM) is utilized to observe the surface morphology of NiTi alloy after immersion. The amounts of released Ni ions are measured by inductively coupled plasma mass spectrometry (ICP-MS). The phosphate buffer saline (PBS) solution is also used as an electrolyte to better understand the effects of organic molecules on the corrosion behavior of NiTi alloy.

2. Experimental details

Commercial NiTi alloy (50.7 at.% Ni) with dimensions of 10 mm × 10 mm × 2 mm was used in our experiments as the working electrode. A copper wire was attached to one side of the working electrode by tin solder and mounted in epoxy resin with an exposure area of 1 cm². It was then wet ground with silicon carbide paper, polished with 2 μm diamond paste, and ultrasonically rinsed in acetone, alcohol, and distilled water for 5 min successively before immersing into electrolytes. The electrolytes were FBS (Gibco, Life Technologies AG, Basle, Switzerland) and PBS (pH = 7.40). Before introduction into the electrode cell, FBS was mixed with the PSN antibiotic solution and Nystatin suspension in the ratio of 100:1 ml.

The electrochemical measurements were conducted in a three electrode cell of 50 ml at a constant temperature of 37 ± 0.5 °C. 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 open circuit potential (OCP) of the electrode was continuously monitored for 200 h with interruptions at 20 h and 200 h to measure the EIS at OCP over a frequency range of 1 mHz–100 kHz by means of a sinusoidal perturbation potential amplitude of 10 mV. The Zview 3.1 software was used to analyze the EIS results.

X-ray photoelectron spectroscopy (XPS) was used for chemical analysis of the NiTi surface. XPS spectra were obtained on the Axis Ultra, Kratos (UK) using monochromatic Al Kα radiation (150 W, 15 kV, 158.66 eV). The pressure in the analytical chamber was 10⁻9 Pa. The binding energies were calibrated relative to the C 1s peak (284.8 eV) from hydrocarbons adsorbed on the surface of the samples. Depth profiles were acquired using 4 kV Ar⁺ ion bombardment with the pressure of 10⁻5 Pa. The sputtered area was 5 mm × 5 mm and the collection area was 250 μm × 250 μm. Three areas were depth profiled to obtain the average film thickness. The place where the concentration of oxygen drops to one half of the maximum concentration near the surface is taken to be the film thickness. To estimate the sputtering rate, a standard SiO₂ sample was analyzed under the same conditions and the sputtering rate was 0.4 nm/min. The survey spectra were obtained at constant pass energy of 160 eV and high-resolution Ti 2p, Ni 2p, C 1s, N 1s and O 1s spectra were recorded at constant pass energy of 80 eV and the XPSpeak 4.1 software was to analyze the XPS data. The background signals were removed by the Shirley mode and processed by Gaussian/Lorentzian (G/L = 4.0) peaks. Field-emission scanning electron microscopy (FE-SEM, JSM-7000F) was utilized to observe the surface morphology of NiTi alloy after immersion at an accelerating voltage 20 kV.

To measure the amount of Ni ions in the electrolyte, the polished and cleaned specimens mounted in epoxy resin with an exposure area of 1 cm² were immersed in a 80-ml polyethylene bottle with 50 ml of FBS and PBS. The bottles were closed tightly and incubated in a thermostatic chamber at 37 ± 0.5 °C for 200 h. Afterwards, the Ni concentration in the electrolyte was determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific Corp, USA). Three parallel samples were used for each group to obtain averages in the experiment.

3. Results and discussion

3.1. Open circuit potential measurements

Fig. 1 shows the evolution of the OCP with time acquired from the NiTi alloy in PBS and FBS solutions. It is clear that the steady state OCP value of the NiTi alloy in FBS is negative to that in PBS. In PBS, the OCP value rises rapidly at the beginning and then gradually slows finally reaching a steady state. In FBS, the OCP value rises rapidly like in PBS but after reaching about 0.425 V, it suddenly decreases rapidly before gradually reaching a steady state.

According to electroneutral theory, during electrochemical reactions, decrease in the anodic dissolution current moves the OCP to the positive direction to balance the cathodic reduction current [17]. During immersion in an electrolyte, the dissolved oxygen adsors on NiTi electrode surface and reacts preferentially with titanium forming a protective film mainly consisting of Ti oxide [5,18] which inhibits the conductivity 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 formation and dissolution of the oxide film is established, a stable anodic dissolution current and therefore a steady OCP value is obtained. The fact that the steady state OCP value in the presence of organics such as proteins is negative compared to inorganic solutions such as PBS and Hank’s’ solution is consistent with previously reported results [9,10,17]. In fact, it has been reported that the adsorption of organics on the electrode can inhibit the transportation of oxygen from the electrolyte to electrode/electrolyte interface, making the Ti oxide film thinner. On the other hand, the proteins in PBS adsorbed on the interface can bind with metal ions and transport them into the electrolyte [8]. Both of them can increase the anodic dissolution current and move the OCP to the negative direction to balance the cathodic reduction current.

![Fig. 1. Evolution of OCP with time recorded for NiTi alloy in PBS and FBS solutions at 37 °C.](image-url)
3.2. Electrochemical impedance spectroscopy measurements

The EIS results obtained from the NiTi alloy in PBS and FBS solutions after different immersion time at OCP and 37 °C are presented as Bode diagrams in Fig. 2. At high frequencies (10^4 to 10^5 Hz), the impedance is almost independent of the frequency with the phase angle approaching 0°. This is the representative response reflecting a resistive behavior and corresponds to the resistance of the electrolyte between the reference and working electrode. In the medium frequency region (10^-2 to 10^4 Hz), the impedance and frequency have a linear relationship, which corresponds to the capacitive behavior of the electrode/electrolyte interface [19]. Only one capacitive behavior can be clearly identified from the NiTi alloy in PBS. However, in FBS, there are three capacitive behaviors. In the low frequency region (10^-5 to 10^-2 Hz), the resistive behavior is observed from the NiTi alloy after 20 h immersion but this is not so after 200 h immersion.

According to the aforementioned analysis, an equivalent circuit is proposed to model the experimental data as shown in Fig. 3. \( R_p \) is the resistance of test electrolyte between the working and reference electrode. In PBS, \( R_p \) corresponds to the resistance of the porous oxide film exterior and \( R_I \) represents the resistance of compact oxide film interior. In PBS, \( R_p \) is the resistance of the oxide film, \( R_{pore} \) is the pore resistance because of the ionic paths across the biofilm, and CPE1, CPE2, and CPE3 are the capacitances represented by the constant-phase elements (CPE). The impedance of CPE can be defined as \( Z_{\text{CPE}} = \frac{1}{(j\omega)^n} \), where \( Z_0 \) is the CPE constant, \( j^2 = -1 \) is the imaginary number, \( \omega \) is the angular frequency and \( n \) is the CPE exponent (\( -1 \leq n \leq 1 \)) [5]. When \( n \) approaches to 1 the CPE can be seen as a nonideal capacitor because of the variable relaxation time induced by the inhomogeneities on the microscopic level at the electrode/electrolyte interface [17]. CPE1 represents the capacitance at the substrate/electrolyte interface, CPE2 corresponds to the capacitance of the thin oxide film, and CPE3 is the capacitance of the biofilm.

Table 1 summarizes the fitted parameters of the equivalent circuit for the NiTi alloy in different solutions after different immersion time. As the positions of the working electrode and reference electrode are fixed during the test, \( R_p \) does not show any obvious difference. In the PBS, \( R_p \) is only \( 1.00 \times 10^{6} \) Ω cm^2 after 20 h immersion but after 200 h immersion, \( R_p \) goes up to \( 3.54 \times 10^{6} \) Ω cm^2, whereas the corresponding capacitance changes from 22.96 μF/cm^2 to 19.04 μF/cm^2, which is indicative of the thickened oxide film and improvement of corrosion resistance.

In FBS, \( R_p \) and \( R_{pore} \) are very small and \( R_I \) is relatively large after 20 h immersion, but after 200 h immersion, \( R_p \) and \( R_{pore} \) become large and \( R_I \) becomes small. The capacitance shows the opposite trend than the resistance. In fact, the capacitance can be expressed as follows [20]:

\[
C_{\text{layer}} = \frac{\varepsilon_r \varepsilon_0 S}{e}
\]

where \( \varepsilon_r \) is the dielectric constant of free space (8.85 \times 10^-12 F/m), \( \varepsilon \) is the relative dielectric constant of the corresponding medium, \( S \) is the surface area of the electrode, and \( e \) is the thickness of the medium. In CPE1 and CPE2, the medium is the oxide film, while in CPE3, it is the biofilm. A large capacitance corresponds to a small thickness of the medium and consequently low resistance. In the beginning, the bio-film is relatively thin and porous, and so inhibition of transportation of oxygen and reaction products is weak as indicated by the small values of \( R_p \) and \( R_{pore} \) as well as high value of \( R_I \). As time elapses, various proteins with different size and shape adsorb onto the surface. The bio-film becomes thicker and less porous thus effectively inhibiting transportation of oxygen and reaction products especially where the bio-film is in close contact with the electrode. At this region, transportation of oxygen from the electrolyte to electrode/electrolyte becomes difficult, making dissolution of the oxide film faster than that of formation speed. As a result, the oxide film becomes thinner, as indicated by the large values of \( R_p \) and \( R_{pore} \) and small \( R_I \) after 200 h immersion compared to 20 h immersion.

The impedance of the oxide film is smaller in FBS (\( R_p + R_I \)) than that in PBS (\( R_p \)) after 200 h immersion as shown in Table 1, but the total impedance in FBS is higher than that in PBS. The result is consistent with previous reports for other biomedical materials [10]. As discussed above, inhibition of transportation of oxygen from the electrolyte to interface due to the bio-film is responsible for the dissolution of the oxide film and reduced impedance. The bio-film itself has a relatively high impedance and so the total impedance increases.

3.3. XPS analysis

In order to obtain more detailed information about the influence of organic species on the corrosion behavior of NiTi alloy, XPS is conducted. The XPS survey spectra acquired from the surface of the NiTi samples after undergoing different treatment are shown in Fig. 4 and the corresponding surface elemental compositions are given in Table 2. The results show that five elements: Ni, Ti, O, C and N are present on the surface of each sample and Ti, O, and C are the dominant surface elements. The C and trace N in Fig. 4a and b arise from organic surface contamination, but in Fig. 4c, they originate from organic contamination and adsorbed organics (such as various proteins) in the FBS. As shown in Table 2, it is clear that the concent-
Concentrations of C and N on the surface of the NiTi alloy after immersion in FBS for 200 h are higher than those on the mechanically polished and PBS immersed sample, thus confirming the presence of adsorbed organics which are composed of C and N primarily.

Fig. 5 shows the Ti 2p XPS spectra of the mechanically polished NiTi alloy as well as the samples after 200 h immersion in FBS and PBS at different sputtering time. As shown in the spectra, there are two peaks corresponding to Ti 2p1/2 and Ti 2p3/2 irrespectively of the sputtering. At the original surface of NiTi alloy, there are two dominant peaks at 465.0 eV and 459.2 eV corresponding to Ti4+ 2p1/2 peak and Ti4+ 2p3/2 peak of TiO2, but the intensity of the mechanically polished one is lower than that after immersion for 200 h. Deeper into the substrate, the Ti0 peak of NiTi immersed in FBS is more obvious than that in PBS at the same sputtering time. After sputtering for 45 min, the main chemical state of Ti in the sample immersed in FBS is Ti0, whereas after sputtering for 60 min, the main chemical state of Ti in the sample immersed in PBS is Ti0. It should be noted that during sputtering, TiO2 can be partially reduced to lower oxides[21]. To monitor this effect, a standard TiO2 sample is also sputtered under the same conditions for comparison as shown in Fig. 5d. It is clear that at the same sputtering time, the NiTi alloy immersed for 200 h contains more Ti3+ and Ti2+ than the standard TiO2 sample, indicating the presence of Ti2O3 and/or TiO in the inner layer of the oxide film. Similar results have been observed on NiTi alloys after heat treatment[21] and Fenton’s oxidation[22]. After the formation of TiO2 on the outermost surface, further oxidation of Ti in the substrate depends on the diffusion of oxygen into TiO2 film. As the TiO2 film becomes thicker, diffusion of oxygen into the substrate is retarded. Insufficient oxidation of Ti induces the formation of suboxides such as Ti2O3 and TiO. Since these suboxides have different Young moduli than TiO2, they may reduce the residual stress in the oxide film[23].

Fig. 6 presents the Ni 2p XPS spectra acquired from the mechanically polished NiTi alloy and samples after 200 h immersion in FBS and PBS at different sputtering time. Almost no Ni can be observed.
Table 1
Fitted parameters of equivalent circuit for NiTi alloy in different solutions with different immersion time.

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Parameters</th>
<th>R s</th>
<th>R p</th>
<th>CPE1</th>
<th>R p</th>
<th>CPE2</th>
<th>R f</th>
<th>CPE3</th>
</tr>
</thead>
<tbody>
<tr>
<td>In PBS 20 h</td>
<td></td>
<td>12.57 ± 0.32</td>
<td>1002 ± 9.1 × 10^{6}</td>
<td>22.96 ± 0.90</td>
<td>0.93 ± 0.00</td>
<td>27.92 ± 1.04</td>
<td>13.30 ± 1.04</td>
<td>9.60 ± 0.67</td>
</tr>
<tr>
<td>Immersed in PBS</td>
<td></td>
<td>12.85 ± 0.10</td>
<td>1502 ± 3.4 × 10^{6}</td>
<td>19.04 ± 0.95</td>
<td>0.90 ± 0.00</td>
<td>164.10 ± 16.49</td>
<td>141.10 ± 16.49</td>
<td>9.91 ± 0.01</td>
</tr>
<tr>
<td>Immersed in FBS</td>
<td></td>
<td>13.60 ± 0.26</td>
<td>1520 ± 3.4 × 10^{6}</td>
<td>0.79 ± 0.02</td>
<td>0.70 ± 0.01</td>
<td>2053 ± 125.6</td>
<td>1963 ± 53.6</td>
<td>10.78 ± 0.01</td>
</tr>
</tbody>
</table>

Table 2
Surface elemental composition (at.%) of NiTi alloy determined by XPS quantification.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni</th>
<th>Ti</th>
<th>O</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanically polished</td>
<td>4.50</td>
<td>19.60</td>
<td>34.54</td>
<td>39.66</td>
<td>1.70</td>
</tr>
<tr>
<td>Immersed in PBS</td>
<td>2.27</td>
<td>22.48</td>
<td>55.58</td>
<td>17.92</td>
<td>2.01</td>
</tr>
<tr>
<td>Immersed in FBS</td>
<td>0.88</td>
<td>6.80</td>
<td>34.21</td>
<td>51.21</td>
<td>6.90</td>
</tr>
</tbody>
</table>

in the outermost surface of the NiTi alloy after 200 h immersion as shown in Fig. 6b, but an obvious Ni0 peak can be detected from the mechanically polished one as shown in Fig. 6a. After sputtering, two peaks centered at 870.5 eV and 853.8 eV emerge corresponding to Ni0 2p1/2 and Ni0 2p3/2. Two small peaks left of the main peaks by ~7 eV can be attributed to the satellite structure of Ni0 2p [24]. As sputtering continues further, Ni0 peaks become more and more obvious, indicating increased Ni concentration in the oxide film. The intensity of the Ni0 peak of the NiTi alloy immersed in FBS is higher than that immersed in PBS for the same sputtering time, indicating the relatively high Ni content. The intensity of the Ni0 peak obtained from the NiTi alloy immersed in FBS after sputtering for 45 min and 60 min is comparable, but that in the sample immersed in PBS is lower. Absence of Ni oxides in the film can be ascribed to its unfavorable Gibbs free energy compared to Ti oxides. Since the standard Gibbs free energy (ΔG°) of NiO, TiO2, and TiO are -211.7 kJ mol⁻¹, -495 kJ mol⁻¹ and -889.5 kJ mol⁻¹, respectively [7], Ti oxide forms preferentially.

The C 1s XPS spectra obtained from the surface of the mechanically polished sample and from the surface of the NiTi alloy after immersion in PBS or FBS for 200 h at different sputtering time are presented in Fig. 7. The curve fitting parameters used for the deconvolution of C 1s spectra are given in Table 3. It is clear that there are only one peak centered at 285.0 eV for the sample of mechanically polished and after immersion in PBS for 200 h. But on the surface of NiTi alloy immersed in PBS for 200 h, it can be deconvoluted into three peaks. The first peak centered at 285.0 eV (C1) is attributed to C–C, C≡C or C–H, the second peak centered at 286.4 eV (C2) is because of the presence of C–N and C–O single bonds, and the third peak at 288.4 eV (C3) is assigned to O=C–O (carboxyl) and
O=C–N (amide groups) bonds [25,26]. However, after sputtering for 2 min, the peaks at 286.4 eV and 288.4 eV, which come from organics in FBS exclusively, disappear and only one peak centered at 285.0 eV arising from carbon contamination during the processing remains, similar to that on the surface of mechanically polished one and the sample after immersion in PBS for 200 h. As sputtering continues, the peak becomes weaker and disappears after 8 min. Fig. 8 shows the N 1s XPS spectra acquired from the surface of the mechanically polished sample and from the surface of the NiTi alloy after immersion in PBS or FBS for 200 h at different sputtering time. Only one peak at 400.3 eV can be observed from all the samples and the intensity of the peak obtained from the mechanically polished sample and that after 200 h of immersion in PBS is comparable. However, the intensity of the peak after immersion in FBS for 200 h is obviously higher because of the adsorption of organics composed of mainly C and N. After sputtering for 2 min, the N signal becomes undetectable indicating disappearance N contaminants and adsorbed organics. Assuming that the N contamination on the surface of the NiTi alloy immersed in PBS is similar to that on the sample immersed in PBS and according to the intensities of C and N peaks on the surface, the atomic ratio N/(C2 + C3) can be determined. For the NiTi sample immersed in FBS for 200 h, N/(C2 + C3) = 0.42 which is close to the theoretical ratio of 0.49 of bovine serum albumin [27] demonstrating that it is composed of predominately organics from the FBS.

**Table 3**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Species</th>
<th>Binding energy (eV)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>C–H</td>
<td>285.0</td>
<td>1.66</td>
</tr>
<tr>
<td>1s</td>
<td>C–N; C–O</td>
<td>286.4</td>
<td>1.66</td>
</tr>
<tr>
<td>0</td>
<td>TiO2</td>
<td>530.5</td>
<td>1.49</td>
</tr>
<tr>
<td>1s</td>
<td>OH–Ti–OH</td>
<td>531.8</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>H3O+–Ti–H2O</td>
<td>533.3</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>C–O</td>
<td>531.0</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>C–O</td>
<td>532.5</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Fig. 7. C 1s XPS spectra obtained from the NiTi samples: (a) surface of the mechanically polished sample; (b) NiTi alloy after immersion in PBS for 200 h; (c) after immersion in FBS for 200 h at different sputtering time: (c1) 0 min, (c2) 2 min, (c3) 4 min, and (c4) 6 min. Fig. 8 shows the N 1s XPS spectra acquired from of the NiTi samples: (a) surface of mechanically polished sample; (b) NiTi alloy after immersion in PBS for 200 h; (c) after immersion in FBS for 200 h at different sputtering time: (c1) 0 min, (c2) 2 min, (c3) 4 min, and (c4) 6 min.

Fig. 9 shows the O 1s XPS spectra acquired from the NiTi alloys including the mechanically polished one and samples immersed in PBS and FBS for 200 h at different sputtering time of 0 min, 2 min, 20 min, 40 min, and 60 min. The curve fitting parameters used for the O 1s peaks are given in Table 3. The O 1s spectra of the outermost surface of the mechanically polished NiTi alloy and the sample immersed in PBS can be deconvoluted into three peaks. The peak centered at 530.5 eV corresponds to oxygen in TiO2 and the two high-energy peaks centered at 531.8 eV and 533.3 eV come from oxygen in Ti hydroxide and hydrated Ti, respectively [26,28]. Similar results have been observed by others [22,29]. On the outermost surface of the mechanically polished sample, the intensity of the Ti hydroxide peak is very low, but after 200 h immersion in PBS, Ti hydroxide becomes the dominant peak, indicating the formation of Ti hydroxide during immersion. After sputtering for 2 min, the hydrated Ti peak disappears and TiO2 becomes the dominant peak. Ti hydroxide is found to be always present in the Ti oxide film albeit at a small fraction. After immersion in FBS, besides the three O 1s peaks aforementioned, two additional peaks emerge on the outermost surface of the NiTi alloy as shown in Fig. 9b. They can be attributed to C=O at 531.0 eV and C–O at 532.5 eV as a result of adsorption of proteins in FBS [29]. After sputtering for 2 min, the peaks of hydrated Ti, C=O, and C–O disappear and TiO2 becomes the dominant peak. During immersion in PBS, Ti hydroxide is also always present in the Ti oxide film but again at a low concentration.

Fig. 10 depicts the XPS depth profiles of the NiTi alloy after immersion in PBS and FBS for 200 h at 37 °C as well as the mechanically polished one. The Ni, Ti, and O signals show the same tendency as sputtering proceeds. After sputtering for 40 min on the immersed sample and 15 min for the mechanically polished one, the Ni and Ti concentrations stabilize gradually to about 60% for Ni and 40% for Ti, which are inconsistent with the chemical composition of untreated NiTi alloy (50.7 at.% Ni). Similar results have been observed by others [7,24,21] and it is attributed to preferential sputtering of Ti. The C signals in Fig. 10a and b come from carbon contamination during sample processing, but the C and N signals in Fig. 10c come from mainly adsorbed proteins which are composed of C and N,
Fig. 9. O 1s XPS spectra of NiTi alloy: (a) on the surface of mechanically polished one (1) and after immersed in PBS for 200 h with different sputtering time: (2) 0 min, (3) 2 min, (4) 20 min, (5) 40 min, and (6) 60 min; (b) after immersed in FBS for 200 h with different sputtering time: (1) 0 min, (2) 2 min, (3) 20 min, (4) 40 min, and (5) 60 min.

Fig. 10. XPS depth profiles of NiTi alloy of mechanically polished (a) and after immersion in PBS (b) and FBS (c) for 200 h at 37°C.
as shown in Figs. 7 and 8. There is no Ni enrichment in all interi-
ors, but the Ni content in the NiTi alloy surface immersed in FBS
is higher than that in PBS. The thickness of the oxide film on the
mechanically polished sample is about 4 nm, which is similar to
that reported by others [30]. After the immersion treatment, the
film thickness reaches about 17 ± 3.0 nm and 10 ± 3.2 nm in PBS and
FBS, respectively. For the oxide film with the same composition, a
thicker film leads to higher impedance, and so the result is consis-
tent with the impedance value measured by EIS. The impedance of
the oxide film in FBS is 3.02 × 10^6 Ω cm^2 which is smaller than that
in PBS (3.54 × 10^6 Ω cm^2).

3.4. Surface morphology

The surface morphologies of the mechanically polished NiTi
alloy as well as the samples after immersion in PBS and FBS for 200 h
at 37 °C are shown in Fig. 11. There is no obvious difference between
the mechanically polished sample and that after 200 h immersion.
in PBS, indicating that corrosion of the NiTi alloy in PBS is limited during that time. However, after immersion in FBS for 200 h, pitting corrosion occurs as indicated by the arrows in Fig. 11c because of breakdown of the protective film. The pits vary in shape but are very small with an average diameter of approximately 5 μm because of the exceedingly localized anodic reaction sites. Fig. 11d shows the magnified image of Fig. 11c (the zone surrounded with a black rectangle) and the corresponding EDS results of the pit and matrix alloy are presented in Fig. 11e. Three elements, Ni, Ti, and O, are detected from the two regions but the Ni concentration decreases while the oxygen concentration increases in the pit. The results are consistent with those reported for prolonged immersion of NiTi in a NaCl solution [31]. In the NiTi–PBS and NiTi–FBS electrochemical systems, hydrolysis can occur [28] as follows:

\[
\text{Ti}^{4+} + 4\text{H}_2\text{O} = \text{Ti(OH)}_4 + 4\text{H}^+ \tag{2}
\]

XPS shows the presence of hydroxyl Ti in the oxide film on the NiTi samples after immersion in both PBS and FBS. The hydrogen ions produced lower the pH value near the reaction sites consequently increasing the solubility of oxide film. A pH value as low as 1.5 has been observed experimentally in the reaction sites [11]. In the NiTi–PBS system, hydrogen ions can be easily consumed by the dissolved oxygen because of the absence of the occluder near the reaction sites. However, in the NiTi–FBS system, because of adsorption of organics onto the NiTi surface, it is difficult for the dissolved oxygen to diffuse to the reaction sites where the organic species are in close contact with the NiTi alloy, thereby causing continuous dissolution of the oxide film. Meanwhile, the aggressive chloride ions are attracted by the positively charged Ni ions at the reaction sites to accelerate the dissolution of the alloy therefore pit formation. After the pits form, Ni ions are released from the pits into the electrolytes. At the same time, the remaining Ti reacts with dissolved O forming Ti oxide because of its lower Gibbs free energy compared to Ni oxide as aforementioned. This type of destructive pitting corrosion induces dissolution of the bulk materials into the electrolytes consequently deteriorating the corrosion resistance of the NiTi alloy.

3.5. Leaching of Ni ions

Fig. 12 shows the release of Ni ions from the NiTi alloy after 200 h immersion in PBS and FBS at 37 °C. More Ni ions are released from the alloy in FBS. Similar results are observed for other biomaterials [32–34]. In general, high interface impedance implies good corrosion resistance and therefore less release of ions. However, in different electrolytes, this may be not true. In the anodic process of the electrochemical reaction, metals lose their electrons becoming cations in the electrolyte. In this process, additional energy must be supplied. In fact, the cations are hydrated in an aqueous solution such as PBS to attain the energy drop. The tendency that metals form hydrated cations can be expressed as the electrode potential difference \( \Delta \Phi \) and given as follows [11]:

\[
\Delta \Phi = -\frac{\Delta G}{2F} \tag{3}
\]

where \( \Delta G \) is the energy change in electrochemical process, \( z \) is the charge of ions, and \( F \) is Faraday constant. \( \Delta \Phi \) denotes the potential difference at equilibrium between the hydrated cations in the electrolyte and the corresponding metal atoms in the electrode, which can balance the energy change \( \Delta G \) in the electrochemical process [11]. In a physiological environment such as FBS, there are not only inorganic species but also many organic species such as proteins. It has been reported that metal ions such as \( \text{Cr}^{3+}, \text{Co}^{2+} \) and \( \text{Ni}^{2+} \) can bind with serum proteins [35] and form organic complexes [8]. When the complexes have lower energy than hydrated cations formed in an inorganic electrolyte such as PBS, \( \Delta G \) is higher and the potential difference \( \Delta \Phi \) becomes lower, while the corrosion current \( I \) is \( \Delta \Phi/R \), where \( R \) is the interface impedance of the electrode. Although the interface impedance in FBS is higher than that in PBS, if the increase percentage of \( \Delta \Phi \) is bigger than that of \( R \), the corrosion current will increase. In the NiTi–PBS and NiTi–FBS electrochemical system, the OCP in Fig. 1 confirms the above analysis. Since the OCP in FBS is negative to that in PBS, the corrosion current is bigger in FBS. That is, in per unit time, the amount of charged Ni ions that cross the oxide film and come into the electrolyte is bigger in FBS than in PBS. On the other hand, breakdown of the oxide film and subsequent occurrence of pits accelerate leaching of Ni ions.

4. Conclusion

Our results show that the presence of FBS can accelerate the corrosion of NiTi alloy. The OCP in FBS is more negative than in PBS. According to the EIS analysis, the oxide film formed in FBS is thinner and more porous than in PBS. The total interface impedance in FBS is bigger than that in PBS because of the formation of the bio-film on the NiTi surface in FBS. XPS shows that the composition of the oxide film formed in FBS is not changed compared to that immersed in PBS. Hydrated Ti is observed on the outermost surface of the NiTi alloy and a small amount of Ti hydroxide is always present in the Ti oxide film. The thickness of the oxide film on the NiTi alloy immersed in PBS and FBS is 17 ± 3.0 nm and 10 ± 3.2 nm, respectively and consistent with EIS results. Pits emerge after immersion in FBS for 200 h because of breakdown of the oxide film accelerating the deterioration of the corrosion resistance of the NiTi alloy, but no pits are detected on the sample immersed in PBS. More Ni ions are released from NiTi alloy in FBS than in PBS during the time monitored because the metal/protein complex formed in FBS has lower free energy than hydrated cations formed in PBS and the occurrence of pits on the NiTi alloy in FBS. Based on our results, it is not sufficient to assess the corrosion resistance of biomaterials in different electrolytes only using the interface impedance. Since there are distinct differences in the corrosion behavior in PBS and FBS, an organic electrolyte such as FBS is recommended instead of an inorganic electrolyte such as various SBF when conducting corrosion resistance evaluation of biomaterials.

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