Corrosion resistance, surface mechanical properties, and cytocompatibility of plasma immersion ion implantation–treated nickel-titanium shape memory alloys


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Abstract: Nickel-titanium shape memory alloys are promising materials in orthopedic applications because of their unique properties. However, for prolonged use in a human body, deterioration of the corrosion resistance of the materials becomes a critical issue because of the increasing possibility of deleterious ions released from the substrate to living tissues. We have investigated the use of nitrogen, acetylene, and oxygen plasma immersion ion implantation (PIII) to improve the corrosion resistance and mechanical properties of the materials. Our results reveal that the corrosion resistance and mechanical properties such as hardness and elastic modulus are significantly enhanced after surface treatment. The release of nickel is drastically reduced as compared with the untreated control. In addition, our in vitro tests show that the plasma-treated surfaces are well tolerated by osteoblasts. Among the three types of samples, the best biological effects are observed on the nitrogen PIII samples. © 2005 Wiley Periodicals, Inc. J Biomed Mater Res 75A: 256–267, 2005

Key words: nitinol; ion implantation; biocompatibility; corrosion; hardness

INTRODUCTION

Nickel-titanium (NiTi) shape memory alloys are promising materials for surgical implants in orthopedics because of their unique shape memory effects and super-elasticity that other common orthopedic materials such as stainless steels and titanium alloys do not possess. Their mechanical properties are also closer to those of cortical bones than stainless steels and titanium alloys. In terms of wear resistance, the materials are better than CoCrMo alloys used in bone trauma fixation. Several other favorable properties of the materials have also been investigated and good biocompatibility has been reported. However, some negative effects have also been pointed out. For example, Berger-Gorbet et al. have found that the osteogenesis process and osteonectin synthesis activity in NiTi alloys are unfavorable compared with stainless steels and titanium alloys. Jia et al. revealed that the cell death rate was severe on NiTi alloys. These problems are believed to stem from the poor corrosion resistance of the materials thereby leading to an increase of the cytotoxicity. It is likely that some toxic components released from the substrate cause the cell death rather than apoptosis. Shih et al. reported that the supernatant and corrosive products from NiTi may result in the death of smooth muscle cells, especially when the amount of released nickel is higher than 9 ppm. A few other studies have reported that nickel ions leached from the alloys cause al-

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TABLE I

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NiTi Without Implantation (Control)</th>
<th>NiTi With Nitrogen Implantation</th>
<th>NiTi With Acetylene Implantation</th>
<th>NiTi With Oxygen Implantation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas type</td>
<td></td>
<td>N₂</td>
<td>C₂H₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Radio-Frequency (RF)</td>
<td></td>
<td>1000</td>
<td>—</td>
<td>1000</td>
</tr>
<tr>
<td>High voltage (kV)</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pulse width (μs)</td>
<td></td>
<td>—</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td></td>
<td>50</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Duration of implantation (min)</td>
<td></td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Base pressure (Torr)</td>
<td></td>
<td>240</td>
<td>90</td>
<td>240</td>
</tr>
<tr>
<td>Working pressure (Torr)</td>
<td></td>
<td>7.0 × 10⁻⁶</td>
<td>1 × 10⁻⁵</td>
<td>7.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Dose (cm⁻²)</td>
<td></td>
<td>6.4 × 10⁻⁴</td>
<td>2.0 × 10⁻⁶</td>
<td>6.4 × 10⁻⁴</td>
</tr>
<tr>
<td>Annealing pressure (Torr)</td>
<td></td>
<td>9.6 × 10¹⁶</td>
<td>5.5 × 10¹⁶</td>
<td>1.0 × 10¹⁷</td>
</tr>
<tr>
<td>Annealing temperature (°C)</td>
<td></td>
<td>8.0 × 10⁻⁶</td>
<td>1.0 × 10⁻⁵</td>
<td>8.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Duration of annealing (h)</td>
<td></td>
<td>450</td>
<td>600</td>
<td>600</td>
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<tr>
<td>Young's Modulus (GPa)</td>
<td></td>
<td>—</td>
<td>—</td>
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</tbody>
</table>

MATERIALS AND METHODS

Preparation of materials

Circular NiTi bars with 50.8% Ni (SE508; Nitinol Device Co., Fremont, CA) were cut into discs of 5 mm in diameter and 1 mm in thickness. They were ground, polished to a shiny surface, and then ultrasonically cleaned with acetone and ethanol before implantation was conducted in our plasma immersion ion implanter. The implantation parameters are displayed in Table I. All the treated samples were ultrasonically cleaned again after PIII.

Depth profile and surface-hardness analysis

The elemental depth profile and surface chemical composition of the plasma-treated samples were determined by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5802 system (Physical Electronics, Chanhassen, MN). The energy of the Ar ion beam was 4 keV and the sputtered area was 2 × 2 mm. Because of the coarse surface, it was very difficult to measure the sputtered depth directly. Therefore, the depth scales in the depth profiles were approximated by using a sputtering rate of 22.6 nm/min calibrated by a SiO₂ source under similar conditions.

The surface hardness of all the samples was measured by nano-indenteter (MTS Nano Indenter XP, Oak Ridge, TN). Nano-indentation tests were conducted on five randomly selected areas to determine the average hardness and Young’s modulus of the treated and control samples.

Corrosion-resistance testing

Electrochemical tests were conducted to evaluate the corrosion-resistance properties of the surface-treated and untreated samples. Tests based on ASTM G5-94 (1999) and G61-86 (1998) were performed using a potentiostat (VersaStat II EG&G, Trenton, NJ) in a standard simulated body...
fluid (SBF) at a pH of 7.42 and temperature of 37°C ± 0.5°C. The solution was prepared by using analytically pure reagents and deionized water. The ion concentrations in the SBF are listed in Table II. The surface area for each sample was 0.181 cm². A cyclic potential spanning between −400 and +1600 mV was applied at a scanning rate of 600 mV per hour. Before the electrochemical tests, the medium was purged with nitrogen for 1 h to remove dissolved oxygen and nitrogen purging continued throughout the measurements.

**Ion-leaching analysis**

Nickel and/or titanium ions leached from the substrates during the electrochemical tests were determined to assess the effectiveness of the plasma-treated surface to impede out-diffusion from the substrate. The solutions taken from each sample after the corrosion test were analyzed for Ni and Ti concentrations using inductively coupled plasma mass spectroscopy (ICPMS) (PE SCIEX ELAN 6100; PerkinElmer, Norwalk, CT).

**Surface-morphology analysis after corrosion test**

To evaluate the surface morphology of the nitrogen-, acetylene-, and oxygen-implanted samples, electrochemical tests were performed on another but similar set of samples. We aimed at comparing the surface morphologies of the exposed and unexposed areas in the same sample. The unexposed area was coated by using a commercial nail polish that was removed by acetone after the test. The surface morphologies of each sample before and after the electrochemical test were studied using scanning electron microscopy (JEOL JSM-820, Japan).

**Cell culturing using cultured osteoblasts**

To investigate the cytocompatibility of the plasma-treated and untreated samples, osteoblasts isolated from calvarial bones of 2-day-old mice that ubiquitously expressed an enhanced green fluorescent protein (EGFP) were used, and cultured in Dulbecco’s modified Eagle medium (Invitrogen) supplemented with 10% (v/v) fetal bovine serum (Biowest, France), antibiotics (100 U/mL penicillin and 100 µg/mL streptomycin), and 2 mM L-glutamine at 37°C in an atmosphere of 5% CO₂ and 95% air. The specimens (1 mm thick and 5 mm in diameter) were fixed onto the bottom of a 24-well tissue culture plate (Falcon) using 1% (w/v) agarose. A cell suspension consisting of 5000 cells was seeded onto the surface of the untreated NiTi samples, the three types of plasma-implanted samples (oxygen, nitrogen, and acetylene) and wells without any metal discs serving as a control for normal culturing conditions. Cells were grown in 1 mL of medium and changed every 3 days. Cell attachment was examined after the second day of culture, and cell proliferation examined after 4, 6, and 8 days of culture. Four samples were taken at each time point for statistical analysis. In our study, cells were allowed to reach confluence during the examination period. To determine the cell number, the attached cells were released by digestion with trypsin–ethylenediaminetetraacetic acid (Invitrogen) and counted using a hemacytometer (Tiefe Profondeur, Marienfeld, Germany). Cell viability was assessed by staining with 0.2% Trypan blue (Sigma). The number of cells was expressed as a mean value ± standard deviation (SD). The data were analyzed by using unpaired two-sample t test, and the statistical analysis was performed using the SPSS program (SPSS for Windows, release 11.0.0).

The attached living EGFP-expressing osteoblasts were visualized using a fluorescent microscope (Axioplan 2; Carl Zeiss, Oberkochen, Germany) with a 450- to 490-nm incident filter and the fluorescence images emitted at 510 nm captured using a Sony DKS-ST5 digital camera.

## RESULTS

**Depth-profile analysis**

The elemental depth profiles of the untreated NiTi, nitrogen-, acetylene-, and oxygen-implanted samples are shown in Figure 1(a–d), respectively. The profiles have been plotted on a depth scale based on a sputtering rate calculated from a SiO₂ reference under similar conditions. Because the sputtering rate changes in the surface region and is different from that of SiO₂, the thicknesses of the implanted zone are approximate, but comparison among different samples is more valid.

Figure 1(a) shows the absence of a transitional layer before PIII treatment and Figure 1(b) shows that a 100-nm-thick titanium nitride surface layer is formed. X-ray diffraction and high-resolution XPS analyses (spectra not shown) reveal that TiN is the only secondary phase present in the N-implanted layer. With regard to the acetylene-implanted layer, a titanium carbide layer with increasing Ti to C stoichiometric ratios is detected underneath the surface oxide layer.

### Table II

<table>
<thead>
<tr>
<th>Ion Concentration of SBF in Comparison With Human Blood Plasma</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>HPO₄²⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBF (mM)</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>4.2</td>
<td>148.5</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Blood plasma (mM)</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>27.0</td>
<td>103.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 1(c) shows a 75-nm-thick titanium carbide layer beneath a 25-nm surface oxide. The titanium chemical states are analyzed using high-resolution XPS and oxides of Ti$^{2+}$, Ti$^{3+}$, and Ti$^{4+}$ are found in the implanted layer. Our results show that a titanium oxide layer approximately 120-nm thick beneath a 25-nm surface oxide is formed after the treatment [Fig. 1(d)]. It should be noted that, in all cases, the nickel contents are suppressed to low levels in the near surface compared with the untreated NiTi control [Fig. 1(a)].

Surface-hardness analysis

Nano-indentation was applied to examine the hardness and Young’s modulus of the untreated control and treated samples’ surfaces. The hardness and the modulus profiles of the control, nitrogen-, acetylene-, and oxygen-implanted samples are shown in Figure 2(a–d), respectively, and the results are summarized in Table III. The hardness of the control sample is 4.5 GPa and the Young’s modulus is 57 GPa. All the surface-treated samples possess higher surface hardness and Young’s modulus than the control.

In the nitrogen-implanted sample, the maximum hardness is 11 GPa at 40 nm from the surface. It gradually decreases to 5 GPa at 165 nm. The Young’s modulus, being about 150 GPa at the topmost surface, decreases to 70 GPa gradually with depth. In the acetylene-implanted sample, the maximum hardness is 9.5 GPa at approximately 30 nm from the surface and gradually diminishes to 4.5 GPa at 150 nm. The Young’s modulus exhibits the maximum value of 110 GPa at the topmost layer and then decreases gradually to a rather constant value of 70 GPa between 110 and 150 nm from the surface. The lower hardness value in the first 30 nm of this sample is probably the result of surface moisture or oxide. In the oxygen-implanted sample, the modulus is 150 GPa near the surface and progressively decreases to 55 GPa between 130 and 160 nm. The hardness is 9 GPa at 20 nm decreasing to 3.5 GPa at 160 nm. It should be noted that these values are higher than that of the control sample of 57 GPa. Our results suggest that the Young’s modulus of the nitrogen-implanted sample is 163% and higher than that of the substrate, whereas the hardness is 144% and 11% higher throughout the measurement. Hence, the nitrogen-implanted sample is mechanically stronger than the substrate. With regard to the acetylene-implanted sample, the hardness of the treated layer between 20 and 150 nm is 110% and 11% greater than

Figure 1. Depth profiles of NiTi alloy (a) without surface treatment, (b) after nitrogen PIII treatment, (c) after acetylene PIII treatment, and (d) after oxygen PIII treatment.
Figure 2. Hardness and modulus profiles of NiTi alloy (a) without surface treatment, (b) after nitrogen PIII treatment, (c) after acetylene PIII treatment, and (d) after oxygen PIII treatment.
that of the substrate, whereas the Young’s modulus is 92% and 23% higher throughout the depth of the measurement. In the oxygen-implanted sample, the hardness at 20–70 nm is 100% and 11% higher and the modulus at 0–120 nm is 163% and 5% higher than that of the untreated substrate. Thus, the mechanical properties of all the treated layers are more superior than those of the untreated substrate.

Corrosion-resistance analysis

Table IV lists some of the essential readings from our electrochemical tests in lieu of the more complicated potentiodynamic curves. $E_{\text{corr}}$ and $E_b$ represent the corrosion potential and the breakdown potential, respectively. Higher $E_{\text{corr}}$ and $E_b$ values represent better corrosion resistance. The $E_{\text{corr}}$ and $E_b$ values of the control sample are $-231$ and $272$ mV, respectively. The $E_{\text{corr}}$ values measured from the nitrogen-, acetylene-, and oxygen-implanted samples are $-163$, $-114$, and $-27$ mV, respectively. The $E_b$ values of the nitrogen-, acetylene-, and oxygen-implanted samples are $1120$, $1170$, and $867$ mV, respectively. All the surface-treated samples exhibit higher $E_{\text{corr}}$ and $E_b$ values than the untreated sample. These results suggest that the corrosion resistance of the implanted samples is enhanced.

Ion leaching from the substrate

Table V displays the amounts of Ni leached from the surface-treated and untreated samples after the electrochemical tests, as determined by ICPMS. The Ni and Ti concentrations in the control sample are 30.2324 and 0.1575 ppm, respectively. The Ni concentrations in the nitrogen-, acetylene-, and oxygen-implanted samples are only 0.0117, 0.0082, and 0.0123 ppm, respectively. With regard to the Ti concentration, it is 0.0527 and 0.0057 ppm in the nitrogen- and acetylene-implanted samples, respectively. The Ti concentration in the oxygen-implanted sample is undetectable. Our results reveal that the amounts of Ni leached from all the treated samples are significantly reduced. The leached amount is only about 0.03 to 0.04% of that of the control samples.

The surface morphologies of the samples after the electrochemical tests are shown in Figure 3. The diameter of the holes on the treated samples’ surfaces is about 25–30 μm, whereas much bigger holes with irregular shapes are found on the control sample surface. It unequivocally shows that the surface treatments can effectively enhance the anticorrosion capabilities.

Cell viability analysis

All the plasma-implanted samples are well tolerated by the EGFP-expressing osteoblasts as shown in Figure 4. After culturing for 2 days, the cells started to attach to and proliferate on all the samples. After 4 days, cell proliferation on the untreated NiTi alloy samples was slightly higher than that of the nitrogen, oxygen, and acetylene PIII samples. However, the nitrogen PIII samples exhibited the highest degree of cell proliferation among the samples after 6 and 8 days of culturing. Cell proliferation on the acetylene- and oxygen-implanted samples was slightly lower than that on the NiTi control sample after 6 and 8 days, but the difference was not significant. A small number of dead cells emerged after 8 days of culturing. The total number of viable cells observed on the untreated, nitrogen, acetylene, and oxygen PIII samples after 2 and 8 days of culturing are shown in Figures 5 and 6, respectively. These results

### TABLE III

<table>
<thead>
<tr>
<th></th>
<th>NiTi</th>
<th>NiTi Implanted With Nitrogen</th>
<th>NiTi Implanted With Acetylene</th>
<th>NiTi Implanted With Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>57</td>
<td>150–65</td>
<td>110–70</td>
<td>150–55</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>4.5</td>
<td>11–5</td>
<td>9.5–4.5</td>
<td>9–3.5</td>
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</table>

### TABLE IV

<table>
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<tr>
<th></th>
<th>Control</th>
<th>N-Treated</th>
<th>C-Treated</th>
<th>O-Treated</th>
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<tr>
<td>$E_{\text{corr}}$ (mV)</td>
<td>$-231$</td>
<td>$-163$</td>
<td>$-114$</td>
<td>$-27$</td>
</tr>
<tr>
<td>$E_b$ (mV)</td>
<td>272</td>
<td>1120</td>
<td>1170</td>
<td>867</td>
</tr>
<tr>
<td>Surface area (cm²)</td>
<td>0.181</td>
<td>0.181</td>
<td>0.181</td>
<td>0.181</td>
</tr>
</tbody>
</table>

### TABLE V

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni Content (ppm)</th>
<th>Ti Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>30.2324</td>
<td>0.1575</td>
</tr>
<tr>
<td>N-treated</td>
<td>0.0117</td>
<td>0.0527</td>
</tr>
<tr>
<td>C-treated</td>
<td>0.0082</td>
<td>0.057</td>
</tr>
<tr>
<td>O-treated</td>
<td>0.0123</td>
<td>Not detectable</td>
</tr>
</tbody>
</table>
clearly demonstrate that cells can attach to and proliferate on the surfaces of all the samples tested, indicating that there is no immediate cytotoxic effects.

**DISCUSSION**

Several surface coatings or surface modification schemes have been studied to enhance corrosion resistance. For instance, Liu et al.\(^4\) reported that the deposition of a TiO\(_2\) film on NiTi alloys using the sol–gel technique improved the anticorrosion properties. However, the surface mechanical properties were not reported. Therefore, the practicality of the use of a coating is questionable if the materials are to be used in orthopedic implants where fretting and abrasive wear are expected. Alternatively, Villermaux et al.\(^5\) studied the use of excimer laser surface treatment to improve the anticorrosion properties of NiTi alloys. This method was shown to reduce the numbers of corrosion pits and sizes and increase the thickness of the oxide layer. However, the biological effects of the materials were not evaluated. Recently, PIII has been used for surface modification of biomaterials. Cheng et al.\(^6\) implanted tantalum by PIII into NiTi substrate. They reported that the treated surfaces possessed better corrosion resistance. Although tantalum is well compatible with living tissues, the price for this uncommon metal is high. Therefore, alternatives have been explored.

It was found that the oxygen-implanted NiTi alloys possessed better corrosion and wear resistance than the untreated NiTi alloys. Our results are similar to the findings of Tan et al.\(^7\) Poon et al.\(^8\) also pointed out that oxygen PIII could significantly reduce the Ni leaching of NiTi alloys. Regarding the acetylene-implanted sample, the mechanical prop-

![Figure 3](image1.png)

**Figure 3.** Microscopic view of the treated and untreated NiTi samples after electrochemical testing under scanning electron microscopy examination. (A) NiTi alloy without surface treatment, (B) with nitrogen PIII implantation, (C) with acetylene PIII implantation, and (D) with oxygen PIII implantation.

![Figure 4](image2.png)

**Figure 4.** Cell proliferation versus number of days. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
Properties and biocompatibility shown in our study are consistent with Mitura et al.’s study of the mechanical properties and biocompatibility of titanium alloys after carbon plasma deposition. They reported that a TiC layer underneath a carbon layer was found after treatment. Therefore, the mechanical strength of titanium alloys was enhanced and that TiC layer was shown to be biocompatible.

Nitrogen is the most common impurity in stainless steel, Ti6Al4V, and aluminum alloys to enhance their mechanical properties and corrosion resistance. In our experiments, the NiTi alloy with a TiN layer had lower dissolution currents, higher corrosion resistance, and higher wear resistance than the untreated NiTi alloy. Again, our results are in line with the results obtained by Wan et al. in their study of TiN and Ti-O/TiN films fabricated by PIII&D on Ti6Al4V substrate. Additionally, preliminary results show that the newly formed surface layers by PIII do not affect the bulk transformation characteristics of NiTi shape memory alloys such as shape memory effect and superelasticity.

The results reported herein suggest that oxygen, nitrogen, or acetylene PIII can effectively suppress the leaching of nickel from the NiTi alloys, as shown in Table V. In our previous immersion tests, the plasma-treated and control samples were immersed in SBF for several weeks at 37°C to simulate in vivo conditions. The amount of Ni leached from the treated NiTi to the SBF was found to be reduced by several orders of magnitude compared with the untreated control. In this new study, we accelerated surface corrosion by applying a high voltage, and the new results are similar, indicating that the barrier against Ni out-diffusion introduced by our plasma treatment is indeed very strong and can withstand both simulated in vivo and accelerated conditions. The enhancement phenomenon can be attributed to the high affinities of Ti toward N, C, and O as compared with Ni under high-temperature annealing. It provides a driving force to enrich the surface with the element forming a stronger chemical bond. The heat of formation of the lowest titanium oxide is $-913 \text{ kJ mole}^{-1}$ whereas that of NiO is $-244 \text{ kJ mole}^{-1}$. The heat of formation of TiN is $-305.6 \text{ kJ mole}^{-1}$ whereas nickel nitrides such as Ni$_3$N are unstable with respect to TiN. The heat of formation of TiC is $-773 \text{ kJ mole}^{-1}$ whereas NiC is not well established, for the Ni-C phase diagram does not show stable carbides. The term nickel carbide may only stand for interstitial solid solutions of C in Ni which possess the NaCl structure. Therefore, the formation of titanium oxide, nitride, and carbide is energetically favored over the nickel counterparts and this is believed to account for the suppression of Ni in

**Figure 5.** Microscopic view of the treated and untreated NiTi (control) after 2 days of cell culturing showing the EGFP-expressing mouse osteoblasts. Proliferation clusters are obviously seen on the surfaces. (A) NiTi alloy without surface treatment; (B) with nitrogen PIII implantation, (C) with acetylene PIII implantation, and (D) with oxygen PIII implantation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
the implanted and annealed region. It should be noted that the degree of suppression does depend on the implantation parameters as reported by Tian et al. in their study of the suppression of nickel in the stainless steel surface after nitrogen PIII.

With regard to the hardness and modulus enhancement, our nano-indentation results show that the treated surfaces possess higher Young’s modulus and hardness than the untreated control surface. Hence, the surface mechanical properties of the treated samples are enhanced. The modified surfaces not only possess better corrosion resistance, but also are capable of resisting mechanical shocks. The efficacy of using PIII to strengthen the material’s surface mechanical properties such as hardness and elastic modulus depends on the amorphous matrix composition and the size of precipitates. Additionally, the corrosion resistance seems to be directly proportional to the surface conditions of metals. For instance, smooth surfaces usually give rise to higher corrosion resistance. A crack-free surface is always advantageous because of the reduced chance of localization of corrosive agent. Chemically inert materials such as metal oxides, nitride, or carbide can effectively reduce the permeability of the corrosive agent. The wetting properties also govern the anticorrosion capability of a material.

Compared with the other treated and untreated NiTi alloys, the in vitro cell culture study indicates that the NiTi alloy after nitrogen implantation exhibits good biocompatibility. The cell proliferation rate on nitrogen-treated surfaces seems to be as good if not better than untreated NiTi alloy at the later time points. This finding can be explained by Piscanec et al.’s study. These authors reported the growth of the calcium phosphate phase on TiN-coated titanium implants, but no such activity was observed on the untreated titanium implants. The surface composition analysis revealed that this layer consisted of mixed precipitates of TiO$_x$N$_y$ oxynitride. This coated layer promoted the deposition of Ca ions attributed to negative charges localized on the surface after surface treatment. Therefore, this coating was favorable to the formation of bone-like materials under in vivo conditions. It was believed that the TiO$_x$N$_y$ oxynitride layer also existed on the nitrogen-implanted NiTi alloy.

Although the surface-modified and untreated NiTi alloys exhibit good biocompatibility, several conditions such as surface free energy, surface stress, surface morphology, wettability, as well as interfacial free energy could also affect the rate of cell attachment and proliferation, and more work is being performed in our laboratory to study these factors and
the change of the surface properties after stressing the materials. It should be noted that we have only demonstrated short-term cell viability. It is possible that the nickel or its compounds may penetrate and leach out through the surface barrier layer over a longer time to the detriment of the cells. The long-term effect of these treated NiTi alloys on cell viability is being tested using both in vitro and in vivo studies.

**CONCLUSION**

The mechanical properties and corrosion resistance in NiTi alloys have been improved by conducting C2H2, N, or O PIII. The leaching of Ni and Ti ions is significantly reduced. Cell culture experiments suggest that all the plasma-treated samples are well tolerated by EGFP-expressing osteoblasts. No immediate cytotoxic effects were found. Long-term in vitro and in vivo biocompatibility studies are being conducted.

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**References**


