Surface mechanical properties, corrosion resistance, and cytocompatibility of nitrogen plasma-implanted nickel–titanium alloys: A comparative study with commonly used medical grade materials

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Abstract: Stainless steel and titanium alloys are the most common metallic orthopedic materials. Recently, nickel–titanium (NiTi) shape memory alloys have attracted much attention due to their shape memory effect and super-elasticity. However, this alloy consists of equal amounts of nickel and titanium, and nickel is a well known sensitizers to cause allergy or other deleterious effects in living tissues. Nickel ion leaching is correspondingly worse if the surface corrosion resistance deteriorates. We have therefore modified the NiTi surface by nitrogen plasma immersion ion implantation (PIII). The surface chemistry and corrosion resistance of the implanted samples were studied and compared with those of the untreated NiTi alloys, stainless steel, and Ti-6Al-4V alloy serving as controls. Immersion tests were carried out to investigate the extent of nickel leaching under simulated human body conditions and cytocompatibility tests were conducted using enhanced green fluorescent protein mice osteoblasts. The X-ray photoelectron spectroscopy results reveal that a thin titanium nitride (TiN) layer with higher hardness is formed on the surface after nitrogen PIII. The corrosion resistance of the implanted sample is also superior to that of the untreated NiTi and stainless steel and comparable to that of titanium alloy. The release of nickel ions is significantly reduced compared with the untreated NiTi. The sample with surface TiN exhibits the highest amount of cell proliferation whereas stainless steel fares the worst. Compared with coatings, the plasma-implanted structure does not delaminate as easily and nitrogen PIII is a viable way to improve the properties of NiTi orthopedic implants. © 2007 Wiley Periodicals, Inc. J Biomed Mater Res 82A: 403–414, 2007

Key words: cell viability; osteoblast; surface treatment; stainless steel; titanium; nickel–titanium alloy

INTRODUCTION

Stainless Steels, titanium, and titanium alloys are the most widely used metallic orthopedic materials. Stainless steel is the oldest and most preferred material for internal fixation devices because of its mechanical properties, cost effectiveness, and acceptable biocompatibility.1,2 Commercial titanium and titanium alloys are the best choice for dental and cementless orthopedic implants since they possess superior biocompatibility and corrosion resistance as well as low modulus.3 A new class of materials, nickel–titanium (NiTi) shape memory alloy, has recently attracted much attention due to its distinctive shape memory effect and super-elasticity, which may not be found in stainless steels and titanium alloys. Other favorable properties of this material as medical implants have also been reported.4–16 A number of studies suggest that this material is compatible with living tissues,7,17–27 but adverse effects have also been reported. A study found that the
osteogenesis process and osteonectin synthesis activity in NiTi alloys were unfavorable compared with stainless steels and titanium alloys. Other studies reported that the cell death rate was severe on NiTi alloy. This problem is suspected to stem from the poor corrosion resistance that may lead to an increase in cytotoxicity. The toxic materials released from the substrate result in cell death rather than cell apoptosis. The supernatant and corrosive products from NiTi substrate may result in the death of smooth muscle cells, especially when leached nickel exceeds 9 ppm. Other studies also reported that the nickel ions from the alloys caused detrimental effects to humans, especially for nickel hypersensitive patients resulting in strong allergic reactions. It is known that the corrosion resistance of NiTi alloys can be varied by the material microstructures and surface morphology. Undoubtedly, the corrosion and wear resistance of the materials must be enhanced before this material can be widely used clinically, since fretting at the interface of couplings of orthopedic implants is expected. Some researchers have implanted tantalum and oxygen using plasma-based techniques to improve the surface mechanical properties of NiTi alloy. Our group has also investigated the enhancement of the corrosion and wear resistance of NiTi using plasma surface treatment. Our previous studies showed that the corrosion and wear resistance could be significantly improved by using acetylene, nitrogen, and oxygen plasma immersion ion implantation (PIII). However, a comparative study on PIII-treated NiTi with other common medical grade metals has not been performed based on our knowledge. The objectives of this study are to compare: (1) the surface mechanical properties; (2) the surface chemistry; and (3) osteoblast viability on nitrogen PIII NiTi, untreated NiTi, medical grade stainless steels, as well as Ti-6Al-4V alloys.

### METHODOLOGY

#### Materials preparation

Circular NiTi bars with 50.8% Ni (SE508; Nitinol Device Company, Fremont, CA) were cut into discs of 5 mm in diameter and 1 mm in thickness. They were ground and 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.

Medical grade stainless steel spinal rods (ISOLA System; DePuy Spine) and Ti-6Al-4V alloy spinal rods (Universal Spine System; Synthes), both 6 mm in diameter, were trimmed down to 5 mm diameter and then sliced into 1-mm-thick discs. The samples were ground and polished under the same conditions as those in the preparation of the NiTi discs. All the samples were ultrasonically cleaned with acetone and ethanol before surface composition analysis and cell culturing.

#### Surface chemical composition analysis

The surface chemical compositions were investigated by using the survey scanning mode of X-ray photoelectron spectroscopy (XPS) (PHI 5802 System; Physical Electronics, MN). The survey scans were acquired after Ar ion sputtering to remove interferences from surface contamination. A monochromatic aluminum X-ray source was employed and the sampled area was 0.8 mm in diameter. The scanning step size was 0.8 eV. The energy scale was calibrated using the Cu2p₃ (932.67 eV) and Cu3p (75.14 eV) peaks from a pure copper standard.

#### Electrochemical tests

The electrochemical tests based on ASTM G5-94 (1999) and G61-86 (1998) were performed by a potentiostat (VersaStat II EG&G) using a standard simulated body fluid (SBF) at a pH of 7.42 and temperature of (37 ± 0.5)°C. The ion concentrations in the SBF are shown in Table II. A cyclic potential

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NiTi Without Implantation</th>
<th>NiTi With Nitrogen Implantation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas type</td>
<td>Control</td>
<td>N₂</td>
</tr>
<tr>
<td>RF</td>
<td>–</td>
<td>1000 W</td>
</tr>
<tr>
<td>High voltage</td>
<td>–</td>
<td>–40 kV</td>
</tr>
<tr>
<td>Pulse width</td>
<td>–</td>
<td>30 µs</td>
</tr>
<tr>
<td>Frequency</td>
<td>–</td>
<td>50 Hz</td>
</tr>
<tr>
<td>Duration of implantation</td>
<td>–</td>
<td>240 min</td>
</tr>
<tr>
<td>Base pressure</td>
<td>–</td>
<td>7.0 × 10⁻⁶ Torr</td>
</tr>
<tr>
<td>Working pressure</td>
<td>–</td>
<td>6.4 × 10⁻⁴ Torr</td>
</tr>
<tr>
<td>Dose</td>
<td>–</td>
<td>1.4 × 10⁻⁵ cm⁻²</td>
</tr>
</tbody>
</table>

| Ion Concentration of Saturated Body Fluid in Comparison With Human Blood Plasma |
|---------------------------------|-----------------|-----------------|
| Na⁺   | K⁺   | Ca²⁺ | Mg²⁺ | HCO₃⁻ | Cl⁻ | HPO₄²⁻ | SO₄²⁻ |
| SBF   | Blood plasma |
| 142.0 | 142.0 | 5.0  | 2.5  | 1.5  | 4.2 | 148.5  | 1.0  | 0.5  |
spanning between $-500 \text{ mV}$ and $+1500 \text{ mV}$ was applied at a scanning rate of $600 \text{ mV/h}$. Before the electrochemical tests, the medium was purged with nitrogen for $1 \text{ h}$ to remove dissolved oxygen. A condition potential of $-800 \text{ mV}$ was applied to the samples for $300 \text{ s}$ to remove the outermost surface oxides due to atmospheric oxidation at room conditions. The cyclic potential was scanned after $10 \text{ s}$ of delay time during which no potential was applied. The surface morphology of each sample after the

TABLE III

A Summary of Elements/Compounds Present at the Topmost Surface of the Nitrogen-Treated NiTi and Other Reference Metals Examined by XPS Surface Surveying Scan

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element/Compound Formed on Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated NiTi</td>
<td>TiO (455 eV), TiO$_2$ (458.8 eV), NiO (853.8 eV)</td>
</tr>
<tr>
<td>N-treated NiTi</td>
<td>TiN (456 eV), TiO$_2$ (458.8 eV), NiO (853.8 eV)</td>
</tr>
<tr>
<td>SS</td>
<td>Mo (228 eV), Fe (707 eV), carbide (282 eV), Cr (574.4 eV), NiO (853.8 eV)</td>
</tr>
<tr>
<td>Ti alloy</td>
<td>TiO (455 eV), TiO$_2$ (459 eV)</td>
</tr>
</tbody>
</table>

*aValues given within parentheses indicate binding energies.*
A test was studied using scanning electron microscopy (JSM-820; JEOL, Japan).

Immersion tests

Two samples of each type were immersed in 25 mL of SBF in polypropylene (pp) bottles. The pp bottles were closed tightly and incubated in a thermostatic chamber at \((37 \pm 0.1) \, ^\circ C\) for 5 weeks. All the bottles were shaken gently for a few seconds every 3 days. After 5 weeks, the SBF in the bottles were analyzed by inductively coupled plasma mass spectrometry (ICPMS) (PE SCIEX ELAN6100; Perkin Elmer) to determine the amount of ions leached from each specimen.

Nanoindentation tests

Nanoindentation tests (MTS Nano Indenter XP) were conducted on five areas to determine the average hardness of the samples. Readings were recorded through a depth of 200 nm. A three-sided pyramidal Berkovich diamond indenter was employed.

Cell culture experiments

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 in our culture in a Dulbecco’s Modified Eagle Medium (DMEM) (Invitrogen) supplemented with 10% (v/v) fetal bovine serum (BioWest, France), antibiotics (100 U/mL of penicillin and 100 μg/mL of streptomycin), and 2 mM L-glutamine at \(37^\circ C\) 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 nitrogen-implanted NiTi, stainless steel, Ti alloy, 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 to obtain better statistics. 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-EDTA (Invitrogen) and counted using a haematocytometer (Tiefe Depth 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).

Static surface contact angle measurement

Static contact angle analysis was conducted using the Rame–Hart Goniometer. A 5-μL droplet of 1× DMEM solution (Invitrogen) at room temperature was injected on the sample surfaces. The 1× DMEM solution was used as the contact liquid instead of water or Hank’s solution to better simulate the actual environment for cell adhesion. To get good statistical averages, five measurements were performed on each sample including the untreated NiTi, nitrogen-treated NiTi, stainless steel, and Ti alloy. The data presented here represent the mean values ± SDs of the measurements of the left and right angles of the droplets. The unpaired two-sample t test was performed on the data and the SPSS.

Figure 2. Breakdown potentials of the untreated NiTi, nitrogen-treated NiTi, medical grade stainless steel, and Ti-6Al-4V alloy.
program (SPSS for Windows, Release 11.0.0) was used for statistical analysis.

**Surface roughness and topography analysis**

The surface roughness and topography of untreated and plasma-treated samples were characterized by atomic force microscopy (AFM) (Auto Probe CP; Park Scientific Instruments). The measurement was operated in the contact mode. The scanning area was $1 \times 1 \mu m^2$ under room ambient condition.

**EXPERIMENTAL RESULTS**

**Surface chemical composition analysis**

Figure 1(a–d) reveal the surface chemical compositions of the untreated NiTi, N-PIII NiTi, medical grade stainless steel, and Ti-6Al-4V alloy, respectively. Table III lists the detected elements and compounds derived from their binding energies. The major compounds found in the untreated NiTi samples surface are TiO, TiO$_2$, and NiO. On the nitrogen-implanted surfaces, TiN, TiO$_2$, and small amounts of NiO are detected. However, the depth profiles (data not shown here) of the N-PIII sample suggest that the NiO concentration is quite low compared with that on the untreated NiTi sample. Iron is abundant on the medical grade stainless steel surface (depth profile data not shown here). In addition to small amounts of Cr and Mo, some carbides and NiO are present. On the medical grade Ti alloy samples, TiO and TiO$_2$ are found.

**TABLE IV**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of Leached Ion ($\mu g/L$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Untreated NiTi</td>
<td>–</td>
</tr>
<tr>
<td>N-treated NiTi</td>
<td>–</td>
</tr>
<tr>
<td>SS</td>
<td>–</td>
</tr>
<tr>
<td>Ti alloy</td>
<td>18</td>
</tr>
</tbody>
</table>

The amounts of leached ions from the metals were measured by ICPMS.

$^*$Non detectable.
Corrosion resistance analysis

The essential readings from our electrochemical tests in lieu of the complete potentiodynamic curves are shown on Figure 2. The breakdown potential is designated by $E_b$. Larger $E_b$ values represent better corrosion resistance. The $E_b$ values measured from the untreated NiTi, N-PIII NiTi, and SS sample are 461, 1080, and 422 mV, respectively. No breakdown is observed in the Ti alloy sample under the measurement conditions. Therefore, the corrosion resistance of the four samples in descending order is Ti alloy > N-PIII NiTi > untreated NiTi > SS. The N-PIII samples exhibit higher $E_b$ values than the untreated NiTi and SS samples. These results suggest that the corrosion resistance of the N-PIII samples is better than both the untreated NiTi and SS.

The surface morphologies of the samples after electrochemical tests are shown in Figure 3. The holes on the nitrogen-treated surfaces are very tiny, whereas much bigger holes with irregular shapes are found on the untreated NiTi and SS sample surfaces. No trace of corrosion is observed on the Ti sample. The corrosion resistance of NiTi has been significantly improved after nitrogen plasma treatment. However, its ability to resist corrosion is still not as good as Ti alloy.

Ions leached from the materials

The amounts of ions leached from the untreated, N-PIII, SS, and Ti alloy samples after the immersion tests are listed on Table IV. The ion concentrations are determined by ICPMS. The Ni concentration leached from the untreated sample is 320 µg/L, whereas that from the N-PIII sample is 57.9 µg/L. No Ti ion is found to be leached from the untreated and N-PIII NiTi samples. With regard to the SS sample, the leached Cr concentration is 47 µg/L, Fe 35 µg/L, Ni 22 µg/L, and Mo 3.8 µg/L. In addition to 18 µg/L of Al, there is about 4.2 µg/L of V leached from the Ti alloy. Again, no Ti ion release is observed.

Surface hardness analysis

Nanoindentation is applied to evaluate the hardness (H) of the untreated control and implanted sample surfaces. The hardness profiles of the untreated, N-PIII, SS, and Ti alloy samples are shown in Figure 4 and the results are summarized in Table V.

In the N-PIII NiTi sample, the maximum hardness is 7.7 GPa on the surface. It gradually decreases to 4.5 GPa at a depth of 165 nm. In the untreated NiTi sample, the maximum hardness is 5.2 GPa at around 30 nm from the surface and gradually diminishes to 4.7 GPa at 150 nm. In the SS sample, the hardness exhibits the maximum value of 6.7 GPa at 50 nm from the surface and then decreases gradually to a rather constant value of 5.2 GPa at 200 nm from the...
In the Ti alloy sample, the maximum hardness is found to be 9.2 GPa at 40 nm from the surface and progressively decreases to 6.0 GPa at 200 nm.

Our results suggest that the hardness of the N-PIII surface is generally higher than that of the untreated NiTi substrate at 0–75 nm. Compared with the SS sample, the hardness of the N-PIII layer in the first 25 nm from the surface is higher. However, the hardness of the N-PIII NiTi sample is lower than that of the Ti sample except in the topmost region. In general, the surface hardness of the N-PIII NiTi is more superior than that of the untreated NiTi and SS samples, but inferior to that of Ti.

Cell proliferation analysis

Figure 5 plots the cell proliferation versus number of days and shows that the N-PIII sample is well tolerated by the EGFP-expressing osteoblasts. After culturing for 2 days, the cells start to attach to and proliferate on all the samples except for stainless steel. After 4 days, cell proliferation on the untreated NiTi alloy samples is slightly higher than that of the N-PIII NiTi, SS, and Ti alloy samples. However, the N-PIII samples exhibit the highest degree of cell proliferation among the samples after 6 and 8 days of culturing. Cell proliferation on the SS and Ti alloy samples are significantly lower than that on the nitrogen-treated NiTi and the untreated NiTi control sample after 8 days ($p < 0.05$). The cell proliferation observed on the untreated NiTi, N-PIII NiTi, stainless steel, and titanium alloy samples after 2 and 8 days of culturing are shown in Figures 6 and 7, respectively. It can be clearly observed that cells are attached to and proliferate on all the samples. The results of cell culturing unequivocally demonstrate
that there is no immediate short-term cytotoxic effects on the N-PIII NiTi samples. The stainless steel samples show the least degree of cell proliferation after 8 days of cell culturing. An insignificant amount of dead cells emerges after 8 days of culturing, perhaps due to cell apoptosis.

Surface contact angle analysis

Figure 8 shows the surface contact angles measured from the different surfaces in descending order: stainless steel > titanium alloy > nitrogen treated NiTi > untreated NiTi. The stainless steel sample possesses the largest contact angle of 91.13°, whereas the untreated NiTi has the smallest contact angle of 77.99°. The untreated NiTi and nitrogen-treated NiTi are shown to be potentially more favorable for cell adhesion than stainless steel and Ti alloy (p < 0.05). It seems that the contact angle of the untreated NiTi is slightly superior than that of the N-PIII NiTi. However, the difference is not statistically significant.

Surface roughness and topography measurement

Figure 9(a–d) reveal the surface topographies of the untreated NiTi, nitrogen-treated NiTi, stainless steel, and titanium alloy. The RMS surface roughness values of the untreated NiTi, nitrogen-treated NiTi, stainless steel, and titanium are 1.61, 2.04, 1.61, and 2.42 nm, respectively (Table VI). It seems that the roughness is slightly increased after plasma treatment. However, compared with the surface topographies of the untreated NiTi, stainless steel, and tita-
nium alloy, the nitrogen-treated NiTi demonstrates a very specific pattern on the nanoscale.

**DISCUSSION**

Nitrogen PIII produces a thin layer of TiN on the surface together with a graded interface with the bulk NiTi substrate. In our previous studies, a TiN layer about 120 nm thick was produced by using 200-Hz PIII. In addition to establishing a protective layer against corrosion and wear, this treatment can suppress the surface Ni concentration and reduce the possibility of Ni ion leaching. Poon et al. reported that a higher implantation frequency with postimplantation annealing could enhance the corrosion resistance and reduce the leaching of Ni. Annealing can further suppress the surface Ni content possibly due to the consolidation of titanium nitride and titanium oxide, which have higher heats of formation compared with nickel nitride and nickel oxide. As a result, Ni is segregated away from the surface. The temperature on the specimen surface during 200-Hz PIII can reach as high as 350°C, which may change the super-elastic transition temperature of the shape memory alloy. Thus, in this study, we used a lower pulsing frequency of 50 Hz to achieve a sample temperature of only about 150°C during PIII. Under the lower frequency conditions, the TiN layer is about 60 nm. In spite of a lower nitrogen implant dose, improved corrosion resistance and mitigated Ni out-diffusion can still be observed. Moreover, the surface TiN which can be classified as hard ceramic possesses higher surface hardness compared with the untreated NiTi and SS at the top 25 nm surface region.

Medical grade stainless steels and titanium alloys are the most common implantable materials in medicine. These metals, especially commercial pure Ti and Ti-based alloys, are believed to possess good corrosion resistance and deformability. A number of

![Figure 8. Plot of surface contact angle measurements of the untreated NiTi, nitrogen-treated NiTi, medical grade stainless steel, and Ti-6Al-4V alloy.](image)

![Figure 9. 3-D AFM topograph of the nitrogen-treated NiTi and other reference metals. Scanned area is 1 × 1 μm², and AFM used in tapping mode at 25°C. (a) Untreated NiTi, (b) nitrogen-treated NiTi, (c) medical grade stainless steel, and (d) medical grade Ti-6Al-4V alloy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]](image)
studies show that they are compatible with living tissue. However, it is known that stainless steels contain small amount of nickel (Ni) and chromium (Cr) to enhance the corrosion resistance. Ni is toxic to living tissues and reported to be carcinogenic as well. Furthermore, Cr may cause impairment of osteoblast proliferation and differentiation as well as cytokine release. Our XPS survey reveals that Cr and Ni are detected on the surface of the medical grade stainless steel samples. Immersion test results also confirm out-leaching of these ions. Schmidt et al. and Okazaki et al. also reported that stainless steel had poor corrosion resistance under physiological conditions that resulted into Ni and Cr ions release. These findings may explain the insignificant growth of osteoblast on the stainless steel samples in our study. In order to improve the corrosion resistance of stainless steel, many methods have been investigated to suppress the release of such toxic ions.

The use of NiTi alloy in human implants is still controversial due to its extremely high nickel concentration compared with other medical grade metals such as stainless steel and titanium alloy. Adverse effects, such as nickel ion leaching from implants, have been reported in humans. In vivo and in vitro studies indicate that the rate of cell proliferation on NiTi samples is lower compared with stainless steels and Ti alloys. However, our cell culturing experiments show higher proliferation on untreated NiTi samples than medical grade stainless steel and Ti alloy after 8 days of culturing (p < 0.05). Furthermore, the N-PIII samples show more superior cell results than stainless steel and Ti alloy samples after 8 days of culturing (p < 0.05). In addition to more superior surface mechanical properties, the N-PIII NiTi favors osteoblast proliferation. This phenomenon can be attributed to the growth of the calcium phosphate phase on the surface of TiN-coated titanium implant, whereas such activities do not take place on the untreated titanium implants. Our surface composition analysis reveals that the surface-treated layer consists of the mixed precipitates of TiO₂Nₓ oxynitride. This coating is favorable to bone-like material formation under in vivo conditions. Our cell culturing results also suggest that the N-PIII samples are as good as, if not better than, the untreated NiTi alloy. Czarnowska et al. confirmed our results that the nitriding layer possesses better cell proliferation over the untreated layer with oxide. Regarding the Ti alloy samples, our study suggests that the cell growth on this metal is significantly less than that on the untreated NiTi alloy and N-PIII samples (p < 0.05). The surface composition analysis indicates that a protective and biocompatible layer (TiₓOᵧ) is formed on the surface. However, this layer is not as good as the nitriding layer in terms of cell proliferation. Additionally, our static surface contact angle measurement results indicate that the nitriding-tREATED and untreated NiTi surfaces are more hydrophilic than the SS and Ti alloy. Our results agree with other previous reports that the hydrophilic surface favors cell adhesion and proliferation. Therefore, this may be the explanation of why there no cells are found on SS after 2 days of culturing.

In addition to the surface free energy and surface chemistry, it should be noted that other parameters such as surface roughness may also affect the rate of cell attachment and proliferation. The surface roughness also likely alters the corrosion resistance of the materials. If corrosion resistance is compromised, leaching of metal ions is very possible, thereby lowering the cytocompatibility of the substrate. PIII is a better surface modification technique to improve the corrosion resistance and cell proliferation of medical implants, especially implants with sophisticated shapes. However, it should be mentioned that this study only reveals the short-term cytocompatibility effects on those surface-treated samples. A long-term cytotoxicity test up to a year is necessary prior to subjecting these surface-treated materials to clinical use.

### CONCLUSION

This study reveals that a graded TiN layer is formed on the surface of NiTi alloy after nitrogen PIII. The enhanced surface possesses better corrosion and wear properties than the untreated NiTi and medical grade stainless steel, and the surface properties are comparable to those of Ti alloy. In terms of cytocompatibility, the cell viability on stainless steel and titanium is inferior to that on the untreated NiTi and N-PIII NiTi. Medical grade stainless steels show the least amount of cells. Our data suggest that nitrogen PIII is favorable to osteoblast proliferation. All in all, this new surface-

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**TABLE VI**

Surface Roughness (RMS) of the Untreated NiTi, Nitrogen-Treated NiTi, Medical Grade Stainless Steel, and Ti-6Al-4V Alloy

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated NiTi</td>
<td>1.61</td>
</tr>
<tr>
<td>N-treated NiTi</td>
<td>2.08</td>
</tr>
<tr>
<td>SS</td>
<td>1.61</td>
</tr>
<tr>
<td>Ti alloy</td>
<td>2.42</td>
</tr>
</tbody>
</table>

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modification treatment will advance the implant technology in the biomedical area.

We thank Mr. Wilson W.C. Chan for his expert technical work.

References