Enhanced retained dose uniformity in NiTi spinal correction rod treated by three-dimensional mesh-assisted nitrogen plasma immersion ion implantation


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Owing to the nonconformal plasma sheath in plasma immersion ion implantation of a rod sample, the retained dose can vary significantly. The authors propose to improve the implant uniformity by introducing a metal mesh. The depth profiles obtained with and without the mesh are compared and the implantation temperature at various locations is evaluated indirectly by differential scanning calorimeter. Our results reveal that by using the metal mesh, the retained dose uniformity along the length is greatly improved and the effects of the implantation temperature on the localized mechanical properties of the implanted NiTi shape memory alloy rod are nearly negligible. © 2010 American Vacuum Society.

NiTi shape memory alloys (SMAs) have recently attracted attention as orthopedic materials due to their superelasticity and shape memory effects. However, Ni ions released from biomedical implants made of NiTi to body tissues and fluids in vivo may induce toxic and allergic responses. Therefore, it is necessary to improve the surface properties of biomedical NiTi SMA. Plasma immersion ion implantation (PIII) has been shown to be an effective surface modification technique for samples and components with an irregular shape. Nitrogen PIII is particularly useful in mitigating nickel release from NiTi spinal correction implants used to surgically treat patients suffering from severe scoliosis. The process also improves the surface corrosion resistance and biocompatibility of the NiTi shape memory alloys. However, uniform nitrogen PIII into the NiTi spinal correction rod is difficult because the correction rod has an S shape that gives rise to nonconformal plasma sheath propagation during PIII. The resulting nonuniform ion flux also causes uneven local temperature during implantation which may affect the mechanical properties of the SMA.

In this work, a cylindrical metal mesh is employed to improve the implantation uniformity along the length of the rod. Samples from different locations on the rod after implantation are analyzed by x-ray photoelectron spectroscopy (XPS) to assess the implantation uniformity. Since variations in the local implantation temperature as a result of different ion fluxes impacting various locations along the rod can degrade the shape memory and superelastic properties of NiTi, the transformation behavior of the specimens is also studied using differential scanning calorimetry (DSC) in order to evaluate any aging effects caused by ion implantation.

NiTi SMA rods containing 50.8 at. % Ni with a diameter of 4.8 mm were used in our experiments. In order to carry out the XPS characterization conveniently, 4.8 mm diameter NiTi samples were mounted on holes at various locations along an aluminum rod with a straight or S shape. The holes were cut parallel to the S-shape plane. NiTi samples that are 6 mm long were mechanically ground, polished to a shiny surface texture, and then ultrasonically cleaned with acetone, ethanol, and distilled water prior to mounting into the holes on the aluminum rods. For the S-shape rod, the shiny surface faced outward from the convex surface. Nitrogen PIII was
conducted in the automated multipurpose PIII system at City University of Hong Kong. As schematically depicted in Fig. 1, the straight or S-shape rod was erected from the sample stage enveloped by a grounded cylindrical stainless steel mesh, which served to stop propagation of the plasma sheath. A stainless steel baffle was employed to envelope the metal mesh. The minimum distance between the biased aluminum rod and grounded metal mesh was 30 mm. The aluminum rod and sample stage were rotated at the rate of 6 rpm during implantation to further enhance implant uniformity. A radio frequency power of 100 W was coupled to the implantation chamber through the antenna to sustain the nitrogen plasma. The target holder was connected to a high voltage power modulator. The samples were implanted using -35 kV sample bias, 200 µs pulse width, and 50 Hz repetition frequency for 2 h. The gas flow rate of nitrogen was 40 SCCM (SCCM denotes cubic centimeter per minute at STP), and the vacuum in the implantation chamber was 5.0 mtorr.

### TABLE I. Sample details.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Distance to the sample stage (mm)</th>
<th>Mesh</th>
<th>Shape of the supporting rod</th>
</tr>
</thead>
<tbody>
<tr>
<td>0421-2</td>
<td>42</td>
<td>Yes</td>
<td>Straight</td>
</tr>
<tr>
<td>0421-7</td>
<td>27</td>
<td>Yes</td>
<td>Straight</td>
</tr>
<tr>
<td>0422-2</td>
<td>42</td>
<td>No</td>
<td>Straight</td>
</tr>
<tr>
<td>0422-7</td>
<td>27</td>
<td>No</td>
<td>Straight</td>
</tr>
<tr>
<td>0715-1</td>
<td>45.5</td>
<td>Yes</td>
<td>S shape</td>
</tr>
<tr>
<td>0715-5</td>
<td>28</td>
<td>Yes</td>
<td>S shape</td>
</tr>
<tr>
<td>0715-8</td>
<td>14</td>
<td>Yes</td>
<td>S shape</td>
</tr>
<tr>
<td>0716-1</td>
<td>45.5</td>
<td>No</td>
<td>S shape</td>
</tr>
<tr>
<td>0716-5</td>
<td>28</td>
<td>No</td>
<td>S shape</td>
</tr>
<tr>
<td>0716-8</td>
<td>14</td>
<td>No</td>
<td>S shape</td>
</tr>
</tbody>
</table>

![Fig. 2](image1.png)  
**Fig. 2.** XPS depth profiles acquired from NiTi samples implanted using a straight supporting rod: (0421-2) with mesh, 42 mm height; (0421-7) with mesh, 27 mm height; (0422-2) without mesh, 42 mm height; (0422-7) without mesh, 27 mm height.

![Fig. 3](image2.png)  
**Fig. 3.** Endothermic cycle DSC curves of NiTi samples implanted using the straight supporting rod.

![Fig. 4](image3.png)  
**FIG. 2.** XPS depth profiles acquired from NiTi samples implanted using a straight supporting rod: (0421-2) with mesh, 42 mm height; (0421-7) with mesh, 27 mm height; (0422-2) without mesh, 42 mm height; (0422-7) without mesh, 27 mm height.
The repetition frequency was chosen to be 50 Hz based on a previous study on the retention of the superelastic properties of NiTi. In this work, ten samples were prepared under different conditions, as shown in Table I. The Ni, Ti, N, and O depth profiles were acquired by XPS (PHI 5802, Minnesota, USA). A monochromatic aluminum x-ray source was used and the XPS data were collected from an area of approximately 2 × 2 mm². Based on similar data obtained from silicon substrates, the argon sputtering rate was estimated to be 3.9 nm/min. DSC was employed to evaluate the aging effect. The masses of the DSC samples were between 5 and 25 mg. The heating and cooling rates were 5 K/min.

In this investigation concerning implantation uniformity, that along the axial direction (length) is our primary focus. The implantation uniformity across a straight rod is first investigated. The XPS depth profiles acquired from the NiTi samples affixed at different locations on the straight aluminum rod are displayed in Fig. 2. Samples 0421-2 and 0421-7 designate those implanted with a metal mesh at heights of 42 and 27 mm from the sample stage, respectively, whereas samples 0422-2 and 0422-7 represent those implanted without the metal mesh at heights of 42 and 27 mm, correspondingly. It is observed that the Ni concentration in the region from the surface to the nitrogen peak is quite low. The results can be explained by the formation of Ti–N, which is energetically more favorable than that of Ni–N and subsequent segregation effects. The nitrogen depth profiles obtained from samples implanted using the metal mesh show a quasi-
Gaussian distribution. The atomic concentration peak of samples 0421-2 and 0421-7 is located at about 22 nm, which is smaller than that observed from the sample implanted without the metal mesh. The discrepancy may be explained by the plasma sheath expansion inside the metal mesh during implantation. The pulse width of 200 μs is so long that the plasma sheath expands to and is stopped by the metal mesh. The implantation process thus resembles a beam-line one. Another factor is that since the straight rod is not aligned perfectly parallel to the metal mesh, ions may impact at a glancing angle into the surface.

The retained dose difference between samples 0421-2 and 0421-7 is much smaller than that of samples implanted without the metal mesh. The nitrogen retained doses in the samples implanted without the metal mesh are comparatively large and it is also true for coimplanted oxygen from the residual vacuum. Moreover, the depth profiles exhibit a second peak. The reason may be that during the implantation process, the temperature in the samples implanted without the mesh is much higher than that in samples implanted with the metal mesh. Therefore, sample aging and oxidation become more obvious. Here, the metal mesh plays an important role in controlling the sample temperature in the PIII process. Due to precipitation of the Ni4Ti3 phase, the aging temperature affects the transformation behavior in NiTi SMA's. Consequently, DSC can be employed to evaluate the implantation temperature indirectly. Figure 3 displays the endothermic cycle DSC curves of the NiTi samples. There is nearly no difference in the transformation temperature of samples 0421-2 and 0421-7 indicating that these two specimens have been subjected to a similar aging temperature, although the small mass of sample 0421-2 results in a smaller peak magnitude compared to sample 0421-7. On the other hand, the transformation temperature of samples implanted without the mesh is much higher than that of samples implanted with the mesh. Furthermore, the transformation peak of \( M \rightarrow R \) of sample 0422-2 is more obvious than sample 0422-7. It is because aging at a low temperature results in multiple-stage transformation sequences. The results also suggest that the implantation temperature is higher, closer to the tip of the rod without using the mesh. That is, the implantation temperature increases toward the tip if a mesh is not used. In the presence of the metal mesh, the implantation temperature is comparatively low and implantation is more uniform along the length of the rod.

Investigation of the NiTi samples mounted on the S-shape supporting rod is then conducted and the XPS depth profiles are exhibited in Fig. 4. It should be noted that the S-shape rod resembles the real geometry of a spinal correction rod. The nitrogen atomic concentration peak of the sample implanted using the mesh is located at about 20 nm, which is comparable to the theoretical SRIM value and in good agreement with results acquired from the straight rod. Our results provide proof that the sample temperature during PIII with a mesh is relatively low and no significant diffusion has taken place. Accordingly, the mechanical properties are not expected to be affected by the implantation process. For samples implanted without the mesh, the nitrogen peak is considerably broader. Moreover, the depth profiles show that the higher the samples are positioned along the rod, the larger the nitrogen concentrations are and the narrower the peaks are. The aging effect appears to consolidate the nitrogen atoms to a narrower region as reflected by the DSC data.

In summary, a metal mesh is employed to improve the retained dose uniformity in spinal correction rods. The XPS results indicate that the nitrogen depth profiles determined from samples implanted with the metal mesh are quasi-Gaussian and the retained dose uniformity along the length of the rod with either a straight or S geometry is significantly improved. The DSC results disclose that the implantation temperature without using the mesh is much higher than that with the mesh. The high temperature causes nitrogen diffusion and peak broadening. Although the broader peak may better mitigate nickel outdiffusion from the bulk material, changes in the mechanical properties as a result of the higher temperature may bring about undesirable effects when the materials are used in spinal correction implants.

**ACKNOWLEDGMENT**

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