INTRODUCTION

Since the introduction of nickel-titanium (NiTi) alloy for endodontic files, root canal instrumentation techniques have witnessed a major transformation. Files made from this alloy are biologically acceptable, highly flexible, and considerably stronger in fatigue resistance than stainless steel files\(^1\). Some studies have indicated that canal enlargement occurs significantly faster with the use of NiTi rotary instruments than with hand preparation\(^2,3\). However, despite its increased strength and flexibility, separation is still a concern with NiTi instruments as the latter have been reported to undergo unexpected fracture\(^4\).

The surface of NiTi instruments is in contact with air containing oxygen and carbon. As such, the concentrations of nickel and titanium are expected to increase from the surface toward the center of the instrument\(^5\). Autoclaving processes, especially when repeated, increase the quantity of oxygen present on the surface of NiTi instruments and bring about conditions that reduce their cutting efficiency\(^5,6\). Against this background, several surface engineering techniques have been used to improve the surface hardness and wear resistance of NiTi instruments\(^7,8\). In the same vein, we postulated that thermal nitriding technique could improve the surface characteristics of the instrument, rendering improved wear resistance and cutting efficiency\(^9\).

With NiTi rotary endodontic files, the irregular, tapered, and helically fluted surface poses a significant technical challenge. A conventional beamline ion implantation technique cannot produce a constant thickness and smooth surface for the modified substrate under these conditions. Against this background, a plasma immersion ion implantation technique (PIII) was employed in the present study. This is a non-line-of-sight technique that is able to produce a functionally graded coating on the surface. One important feature of this process is that no divergent interface exists between the bulk substrate and the treated surface layer. This is a critical advantage because the modified surface layer must have the potential to undergo any transformation that the bulk material experiences in order to prevent the occurrence of delamination. The latter often occurs with other conventional coating techniques, although the common goal of all coating techniques is the formation of a titanium nitride layer. With the PIII technique, its additional upperhand advantage is that it is well suited for the surface modification of NiTi rotary instruments.

Keywords: XPS, DSC, plasma immersion ion implantation
alloys. This is because it is carried out at near-room temperature and therefore should not significantly alter the microstructure and bulk properties of the alloy.13

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique with an analysis depth ranging from 2 to 10 nm for photoelectrons with binding energies of 0.1–1100 eV.14–16 The most important advantage of XPS is its ability to resolve shifts in the binding energy of inner-shell electrons when the energy status of valence electrons is changed, owing to alterations in the chemical environment that modify the nuclear attractive force for inner-shell electrons. Thus, XPS can provide information about the bonding state, oxidation state, change in crystal structure, and formation of new compounds.14–16

In addition, recent studies17–20 published in endodontic literature have indicated that the structure of NiTi rotary instruments can be conveniently investigated by differential scanning calorimetry (DSC). With this analytical technique, the difference in thermal power supplied to a test specimen and an inert control specimen heated at the same rate is measured very accurately19,20. Structural transformations in the NiTi alloy are revealed as an endothermic peak on the heating DSC curve and as an exothermic peak on the cooling DSC curve. Thus, DSC can provide information on the temperature ranges and enthalpy changes for the phase transformations of the overall bulk of a specimen.19

The purpose of this study was to investigate the application of PIII for surface modification of the clinically popular ProTaper® NiTi rotary instruments. This investigation was carried out by utilizing XPS and DSC, having mentioned their useful and beneficial features above. More importantly, the PIII method was investigated because it has the potential of developing into a standard surface improvement technique. The hypothesis in this study was that the application of PIII would form a TiN layer on the surface of the specimen without any change in transformation temperature.

MATERIALS AND METHODS

NiTi rotary instruments
A total of 12 ProTaper® F2 (Maillefer, Ballaigues, Switzerland) endodontic NiTi rotary instruments were selected. These as-received instruments were divided into three groups of four instruments each: one control group (Group A) and two experimental groups (Groups B and C) that underwent the PIII surface modification process involving either nitrogen ion implantation or nitrogen ion plus argon ion implantation. The PIII equipment was provided by Metal Industry Research and Development Center (Kaohsiung, Taiwan).

Specimen preparation
To prepare for the PIII processes, the specimens were sputter-cleaned to remove any residual surface contaminants using energetic argon ions at 5 kV. Whole procedure was carried out at a target voltage of 25 kV with an incident dose of 5 × 10¹⁴ ions/cm² for 60 minutes. Cutting surfaces of the instruments were implanted on all sides because the handles of the instruments were secured in the holes of a metal plate during PIII processing.

XPS analysis
Three representative specimen surfaces for each of the three different conditions of NiTi instruments were analyzed by XPS (ESCA-850, Shimadzu, Kyoto, Japan), employing AlKα radiation at 7 kV and 30 mA, under a pressure of 1 × 10⁻⁶ Pa. An argon ion sputtering rate of 0.1 nm/sec was utilized to determine the chemical compositions of the surface and subsurface layers. Each test specimen consisted of three segments, approximately 5 mm in length, placed side by side to compare with and without 180 seconds of argon ion sputtering on the surfaces of three different conditions. A take-off angle of 90° was used for all specimens. Surface composition (at%) was calculated from the relative XPS peak intensity by using a computer software (CasaXPS, Casa Software Co. Ltd.) that took into account variations in atomic sensitivity.15

DSC analysis
DSC analyses (DSC Q100, TA instruments, Wilmington, DE, USA) were performed between -70° and 100° on specimens in the as-received and post-implanted conditions. The original instruments for analysis were cut into segments with a water-cooled, slow-speed diamond saw to minimize mechanical stresses that might change the proportions of the austenitic and martensitic NiTi phases. There were three test specimens for each of the three different conditions of NiTi instruments. Each test specimen consisted of two to four segments, approximately 4 to 5 mm in length, placed in an open aluminum pan; no crimped pan top was used to avoid mechanical stresses on the specimens. An empty aluminum pan served as the inert control specimen for the DSC measurements.16

For each analysis, the specimen was first cooled from room temperature to -70°, then heated from -70° to 100° to obtain the heating DSC curve. Subsequently, the specimen was cooled back to -70° to obtain the cooling DSC curve. Linear heating or cooling rate was a standard 10° per minute for each analysis. The DSC cell was purged with dry nitrogen at a rate of 50 cm³/min.
Temperature calibration of the DSC apparatus was performed with deionized water and indium.

The DSC plots were analyzed by computer software to obtain the peak temperatures for the phase transformations, along with the enthalpy changes associated with these processes. Interpretations of the plots were based on previous DSC studies of NiTi alloys in orthodontics\textsuperscript{19,20} and materials science\textsuperscript{22}, as well as on a study of rotary endodontic instruments for the as-received condition.

**RESULTS**

Figure 1 shows the Ti 2p XPS spectra with and without argon ion sputtering on the surfaces of three different conditions of NiTi instruments. High-resolution XPS spectra of the binding energy regions of Ti 2p\textsubscript{3/2} and 2p\textsubscript{1/2} were collected. In all the XPS plots, spectra without argon ion etching are shown at the top and spectra with argon ion etching (180 seconds) are shown at the bottom. The Ti 2p spectrum was detected in all the specimens and consisted of two major peaks, identified as Ti 2p\textsubscript{3/2} at 458.5 eV and Ti 2p\textsubscript{1/2} at 464.5 eV corresponding to TiO\textsubscript{2}. A relatively small peak at 454.5 eV corresponding to metallic Ti under an oxide film was clearly shown after argon ion sputtering for all the specimens. These tendencies were similar in all the three types of specimens.

Figure 2 shows the Ni 2p XPS spectra with and

![Fig. 1 Ti 2p XPS spectra without (upper) and with (lower) argon ion sputtering for 180 seconds on the surfaces of NiTi rotary instruments: (a) as-received; (b) nitrogen PIII-treated; and (c) nitrogen ion plus argon ion PIII-treated.](image1)

![Fig. 2 Ni 2p XPS spectra without (upper) and with (lower) argon ion sputtering for 180 seconds on the surfaces of NiTi rotary instruments: (a) as-received; (b) nitrogen PIII-treated; and (c) nitrogen ion plus argon ion PIII-treated.](image2)
without argon ion sputtering on the surfaces of three different conditions of NiTi instruments. The major Ni 2p3/2 peak at 853.1 eV observed for all specimens was assigned to metallic nickel in the alloy under the surface film. The small Ni2+ peak at 856.7 eV obtained from the unetched PIII-treated specimens for both ion-implanted specimens could be assigned to Ni3+ in the surface film. The presence of Ni 2p3/2 peak corresponding to metallic nickel for both ion-implanted specimens without argon ion sputtering suggested that the thickness of the surface film was less than the escape depth of photoelectrons (<1 nm). As Ti 2p-corresponding TiO2 had a much higher peak intensity than Ni 2p-corresponding Ni3+, it should be reasonable to suggest the presence of a Ti-rich oxide film on the surface.

Figure 3 shows the N 1s XPS spectra with and without argon ion sputtering on the surfaces of three different conditions of NiTi instruments. For N 1s spectrum of the as-received specimen, a large peak at about 401 eV was observed on the surface, which probably corresponded to the organic matrix of some contaminant. The nitride was no longer detected during the sputtering time. The other large peak at about 396.9 eV corresponding to TiN was clearly seen for both PIII specimens, whereby the intensity of this peak increased with argon ion etching.

Table 1 shows the atomic concentrations of three major elements and the atomic ratio of N/Ti on the surfaces of all the specimens with and without argon ion sputtering. In both types of ion-implanted specimens, the concentration of Ti on the surface before argon ion etching was much higher than that of Ni which meant that a Ti-rich oxide film was formed on the surface. It can also be seen from Table 1 that the concentration of N and the atomic ratio of N/Ti on the surfaces of nitrogen PIII-treated or nitrogen plus argon PIII-treated specimens showed considerably higher values than those of as-received specimens. In other words, a N-enriched surface presumably some form of TiN layer was present. Moreover, the two different PIII methods had similar effects on the atomic ratio of N/Ti. This indicated that a higher concentration of nitrogen ions was not introduced into the surface of specimens via the additional aid of argon ions at a bias voltage.

![Fig. 3 N 1s XPS spectra without (upper) and with (lower) argon ion sputtering for 180 seconds on the surfaces for three different conditions of NiTi instruments shown in Fig. 1: (a) as-received; (b) nitrogen ion PIII-treated; and (c) nitrogen ion plus argon ion PIII-treated.](image)

Table 1 Atomic concentrations of three major elements and atomic ratio N/Ti on the surface of all the representative specimens with and without argon ion sputtering

<table>
<thead>
<tr>
<th>Group</th>
<th>Sputtering time (sec)</th>
<th>Ni 2p</th>
<th>Ti 2p</th>
<th>N 1s</th>
<th>N/Ti ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A (As-received)</td>
<td>0</td>
<td>17.0%</td>
<td>83.0%</td>
<td>0%</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>64.2%</td>
<td>35.8%</td>
<td>0%</td>
<td>0</td>
</tr>
<tr>
<td>Group B (PIII N2)</td>
<td>0</td>
<td>16.5%</td>
<td>75.9%</td>
<td>7.6%</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>44.7%</td>
<td>51.0%</td>
<td>4.3%</td>
<td>0.08</td>
</tr>
<tr>
<td>Group C (PIII N2+Ar)</td>
<td>0</td>
<td>33.9%</td>
<td>61.3%</td>
<td>4.8%</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>52.5%</td>
<td>43.1%</td>
<td>4.5%</td>
<td>0.10</td>
</tr>
</tbody>
</table>
of 25 kV.

Figure 4 shows the DSC plots for the three representative ProTaper test specimens. The heating curve for the as-received instruments contained a single endothermic peak at approximately $2.7^\circ\text{C}$ which corresponded to the transformation from martensitic NiTi to austenitic NiTi with increasing temperature, and which was completed at approximately $15^\circ\text{C}$ (the austenite finish or $A_f$ temperature). The enthalpy change ($\Delta H$) for the overall transformation from martensitic NiTi to austenitic NiTi was $2.3 \text{ J/g}$. The cooling curve in Fig. 4 contained a single exothermic peak at approximately $0.4^\circ\text{C}$ which corresponded to the transformation of austenitic NiTi to martensitic NiTi with decreasing temperature, and which began at approximately $20^\circ\text{C}$ (the martensite start or $M_s$ temperature). The enthalpy change for the overall transformation from austenitic NiTi to martensitic NiTi was $3.0 \text{ J/g}$.

For all the ProTaper specimens, as shown in Table 2, the overall enthalpy change on the heating curve ranged from 2.2 to 2.5 J/g, while the overall enthalpy change on the cooling curve ranged from 2.5 to 3.0 J/g. The temperature ($A_f$) for completion of the transformation from martensitic NiTi to austenitic NiTi on heating ranged from 13° to 29° for the three specimen groups. The approximate starting temperatures ($M_s$) for the transformation from austenitic NiTi to martensitic NiTi ranged from 17° to 23° for the three specimen groups. It was

![Fig. 4 Representative DSC plots showing the heating (lower) and cooling (upper) curves for the three different conditions of ProTaper® specimens: (a) as-received; (b) surface-modified by nitrogen ions using PIII; and (c) surface-modified by nitrogen ions and argon ions using PIII.](image)

<table>
<thead>
<tr>
<th>Property</th>
<th>Group A*</th>
<th>Group B*</th>
<th>Group C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (martensitic NiTi to austenitic NiTi) on heating (J/g)</td>
<td>2.3 - 2.5</td>
<td>2.2 - 2.5</td>
<td>2.2 - 2.3</td>
</tr>
<tr>
<td>$\Delta H$ (austenitic NiTi to martensitic NiTi) on cooling (J/g)</td>
<td>2.5 - 3.0</td>
<td>2.7 - 2.8</td>
<td>2.7 - 2.8</td>
</tr>
<tr>
<td>Peak temperature, martensitic NiTi to austenitic NiTi on heating ($T$)</td>
<td>2.7 - 14.7</td>
<td>2.8 - 7.2</td>
<td>2.8 - 7.1</td>
</tr>
<tr>
<td>Peak temperature, austenitic NiTi to martensitic NiTi on cooling ($T$)</td>
<td>0.4 - 7.4</td>
<td>0.5 - 0.5</td>
<td>2.3 - 0.5</td>
</tr>
<tr>
<td>Approximate completion temperature ($A_f$) for transformation to austenetic NiTi ($T$)</td>
<td>15 - 29</td>
<td>13 - 26</td>
<td>13 - 23</td>
</tr>
<tr>
<td>Approximate start temperature ($M_s$) for transformation to martensitic NiTi ($T$)</td>
<td>20 - 23</td>
<td>18 - 23</td>
<td>17 - 20</td>
</tr>
</tbody>
</table>

*Includes data for two instruments of this group
evident from Table 2 that the temperatures for phase transformations and the resulting enthalpy changes for the PIII-processed instruments were similar to those of the as-received instruments. Consequently, DSC comparisons of the PIII surface-modified NiTi instruments with the control instruments that were not subjected to PIII processing confirmed that the transformation behavior of the bulk NiTi material was not affected.

DISCUSSION

The plasma immersion ion implantation (PIII) technique is an advanced technology, which is capable of creating a diffuse layer into a metal surface. The PIII process differs from other coating techniques that alter the size or dimensions of specimens. The PIII technique utilizes low-pressure gaseous plasma as the source of ionized elements, and negative high-voltage pulses are applied to a conductive substrate that is immersed in the gaseous plasma. With each pulse, an electric sheath forms adjacent to the substrate, and gas ions entering the sheath are accelerated toward and implanted into the substrate. The PIII method is capable of inserting interstitial elements such as nitrogen, oxygen, or carbon into a metal. Oxygen detected in XPS analysis was attributed to the oxygen from a tape used to fix specimens on the specimen holder because it was not employed in micro-ESCA apparatus. On the other hand, argon was not detected in all the specimens. These were the reasons why Table 1 did not include oxygen and argon. Moreover, it should be highlighted that the surface film was not uniformly removed by argon ion sputtering. This was chiefly due to the complicated twisted configuration of the rotary instruments employed in the present study.

In the present study, the objective was to introduce nitrogen ions into the surface of NiTi rotary endodontic instruments more efficiently by utilizing argon ions alongside nitrogen ions. This procedure resulted in the presence of a titanium nitride layer, which was confirmed by XPS, thereby giving the instruments a light golden appearance. However, XPS analysis indicated similar concentrations of N and N/Ti ratios for the two different PIII methods, as shown in Table 1. This observation seemed to indicate that the additional use of argon ions with nitrogen ions during PIII processing did not achieve the anticipated effect within limited sputtering depth. Therefore, utilizing a higher bias voltage would be the better way as a previous study had confirmed. It is important to note that industrial PIII processing can accommodate thousands of rotary instruments in the working chamber, and that the entire process requires less than two hours. Thus, PIII is an advanced technological development worthy of clinical application to endodontics and possibly to other dental material applications where hard coating technology would be worthwhile.

The Ti 2p\(_{3/2}\) peak at 458.5 eV suggested the presence of a TiO\(_2\) layer on all specimen surfaces. Therefore, results of this study confirmed that the presence of TiO\(_2\) resulted from the presence of residual oxygen in the reactive chamber. In addition, minor oxygen species in the ionic or free radical state are recognized as highly reactive species, and the composition of reactive species in non-oxygen plasma may have an effect on the surface properties of a thin PIII-treated layer. As for nitrogen, it is the most common atom in NiTi alloys and stainless steel to enhance their mechanical properties and corrosion resistance. The N 1s peak at 396.9 eV for PIII-treated specimens agreed with published data for pure TiN. With the presence of this TiN layer, the wear properties and corrosion resistance would likely be improved.

At this juncture, it should be mentioned that a TiO\(_2\) or TiN layer can act as a barrier to prevent atomic Ni from being released at the surface. In this manner, this surface layer contributed favorably to the corrosion resistance and biocompatibility of NiTi.

The DSC results showed that all the NiTi rotary instrument specimens analyzed in this study were in a superelastic condition, as found in a previous study for as-received instruments of two brands. The austenite-finish (A\(_f\)) temperature for completion of the transformation from martensitic NiTi to austenitic NiTi on heating was found to be near room temperature for all tested specimens. In addition, temperatures for phase transformations and the resulting enthalpy changes of the bulk materials changed minimally after PIII treatment. Therefore, the present results suggested that application of the PIII technique to rotary NiTi instruments for use in the clinic would not compromise the original beneficial properties of NiTi alloys.

In conclusion, the cutting surfaces of endodontic NiTi rotary instruments can be successfully modified by the non-directional nitrogen PIII method to create a TiN layer, which then gave the instruments a resultant light golden appearance. The PIII technique did not alter the metallurgical phases in the NiTi rotary instruments or their superelastic character, because it was carried out at near-room temperature. Therefore, results of this study suggested that the PIII technique was a feasible way to improve the surface characteristics of NiTi rotary instruments.
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REFERENCES