

# Fabrication Of Hard Coatings On NiTi Instruments

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The present study was designed to compare the nature of modified surface layers obtained by two different procedures on endodontic files made of NiTi alloy: the procedures were arc evaporation physical vapor deposition and thermal metal organic chemical vapor deposition (MOCVD). Experimental samples were GT Rotary Instruments. The first method was based on the physical deposition of elemental titanium in the presence of nitrogen. The second technique is a typical MOCVD procedure which adopts  $Ti(Et_2N)_4$  as a titanium and nitrogen precursor. Control samples were not exposed to any process. The chemical composition of the surface and in-depth layers of each sample were examined by X-ray photoelectron spectroscopy and X-ray diffraction measurements. The instruments showed surface chemical compositions that were different from those seen in the control group; samples treated with the first method show a surface Nitrogen/Titanium ratio of 1; MOCVD instruments show a surface Nitrogen/Titanium ratio of 1.7; control samples show a Nitrogen/Titanium ratio of 0.2. Both techniques can produce a high nitrogen concentration on the surface. However, data showed that the morphologies, the in-depth nitrogen distribution, and the chemical nature of the coatings obtained with the two procedures were different. The paper also reports the effects of the two deposition procedures on the nickel/titanium ratio of the surface.

Root canal preparation has been considered the most important step in root canal therapy. In root canal preparation, the use of rotary nickel-titanium instruments is gaining more acceptance. Therefore, the surface quality of the cutting surfaces and cutting heads after repeated use is of clinical interest (1). A variety of surface engineering techniques have brought about improvements in hardness and wear resistance by the production of hard surface coatings such as titanium nitride (2). Lee et al. (3) implanted doses of  $4.8 \times 10^{17}$  per ion/cm<sup>2</sup> of boron to successfully increase the surface hardness of nickel-titanium instruments. Some authors have increased the surface hardness and the wear resistance of

nickel-titanium instruments through ionic implant and thermal nitridation (4). In both cases, most of the nitrogen is essentially located on the surface, suggesting the presence of layers of  $Ti_2N$  in the case of thermal nitridation or TiN in the case of ionic implantation. Preliminary studies have demonstrated that the metal organic chemical vapor deposition (MOCVD) can be used to increase the Nitrogen/Titanium ratio up to 2 on the surface (5).

Previous studies have shown that the nickel concentration on the surface is also strongly affected by surface treatment. In this respect, the evaluation of the surface nickel amount is important to characterize the chemical composition of NiTi instruments. Shabalovskaya and Anderegg (6) have examined by spectroscopic techniques the NiTi alloy surface exposed to sterilization processes. They noticed that nickel concentration on the surface of the instrument decreases after autoclave sterilization processes. Similarly, it was found that nickel surface concentration is strongly reduced by ionic implantation and thermal treatment under  $N_2$  (4).

The aim of this study was to investigate the applicability of MOCVD in the fabrication of surface layers with different physical and chemical properties (i.e., composition and thickness). Moreover, an alternative method based on the arc physical vapor deposition (Arc PVD) of titanium and nitrogen was tested on rotary endodontic NiTi instruments. The chemical nature of the coatings obtained with the two methods was compared.

## MATERIALS AND METHODS

Two methods of deposition were adopted. The first technique is a MOCVD procedure which deposits  $Ti(Et_2N)_4$  as a titanium and nitrogen precursor (7, 8). Depositions were performed under reduced pressure (1 Torr).  $Ti(Et_2N)_4$  was evaporated at 25°C. The deposition zone was kept at 300°C. The MOCVD deposition system has already been reported in a previous paper (5).

The second method is an arc evaporation physical vapor deposition (PVD) performed by CRT-Milano using ION-BOND® technology (9). In this method, titanium is simultaneously evaporated at microscopically small areas and accelerated all in one single work stage. Deposition was performed under nitrogen at  $10^{-6}$  Torr. Pure titanium was used as the source target. The NiTi instruments were kept at 300°C.

The instruments used for experimental models were 15 GT Rotary instruments 0.6 taper n. 20 (Maillefer, Ballaigues, Switzerland). The instruments were divided into three groups (A, B, and C) of 5 instruments each.

Group A: Samples were treated via MOCVD.

Group B: Samples were treated via PVD.

Group C: Samples were not exposed to any process and were utilized as a control group.

All instruments were analyzed with X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). XRD measurements were made with a Bruker AXS D5005, an X-ray Diffractometer equipped with a copper anode.  $20^\circ < 2\theta < 70^\circ$  scans were used. XPS alternating with sputter etching was used to determine the chemical composition of the surface and near the surface to a depth of 60 nm. XPS analysis was carried out with a PHI ESCA/SAM 5600 Multi Technique system unit (PHI, Ismaning, Germany).

The X-ray source, operating at 350 W, induced the emission of photoelectrons from the sample. Kinetic energies of photoelectrons emitted from the atoms were characteristic for each element. In-depth distribution (depth profile) was obtained by alternating XPS analysis and sputter etching with an argon ion gun operated at 4 KeV. Material was removed by sputter etching at approximately 2 nm per minute (sputter rate). Sputter rate was estimated from theoretic values of nickel and titanium sputter yields.

Before the observation under the SEM, all the instruments were cleaned in an ultrasonic dish and were not autoclaved. The enlargements for all the samples were as follows: I micrograph at  $53/170 \times$  for the apical and middle portion of the instrument; II and III micrographs respectively at  $2400 \times$  and  $5000 \times$  for the surface of the instrument.

## RESULTS

Possible alterations of the crystalline structure of the samples were checked by XRD. XRD patterns of all samples show the typical crystalline phase of NiTi material, thus showing that the deposition processes do not affect the bulk structure of the instruments.

The surface compositions were analyzed by XPS. Results are shown in Fig. 1. The three groups show a different Nitrogen/Titanium ratio. Control group C has a surface Nitrogen/Titanium ratio of 0.2; samples of group A have a surface Nitrogen/Titanium ratio of approximately 1.7; the Nitrogen/Titanium ratio of those of group B is approximately 1. In order to evaluate the nitrogen concentration in the in-depth layers, the XPS analysis was performed after 5 min of sputtering processes. After sputter the Nitrogen/Titanium ratio in control group samples was near 0. The Nitrogen/Titanium ratio of sample of group A decreased markedly to 0.25, whereas group B decreased slightly to 0.9. XPS analysis and sputter etching were also used to evaluate the amount of nickel on the surface and in the in-depth layers.

In Fig. 2 the Nickel/Titanium ratios are reported on the surface and in the in-depth layers. In the control group C the highest value of the Nickel/Titanium surface ratio (0.25) was observed. The lowest surface value (0.1) was observed in group B samples. After sputter the ratio decreased in all samples. Also, the lowest ratio was observed for group B samples in this case.

SEM microphotographs showed that the morphologies of instrument surfaces in groups A and B were slightly changed with respect to group C (Fig. 3). The surfaces of all instruments in groups A appear covered by a deposited material (Fig. 4) with a few small grains embedded in a smooth layer. The surface of instruments in group A appeared homogeneous and flat. The surface of instruments in group B appeared more rough than those in

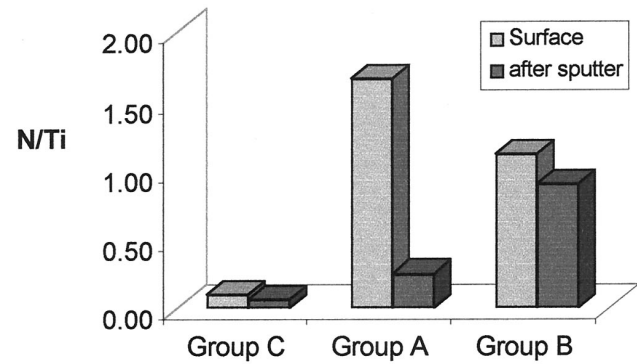


FIG 1. Plot of the atomic nitrogen/titanium on the surface of instruments of groups A, B, and C. Group A: N/Ti ratio = 1.7, group B: N/Ti ratio = 1, group C: N/Ti ratio = 0.2.

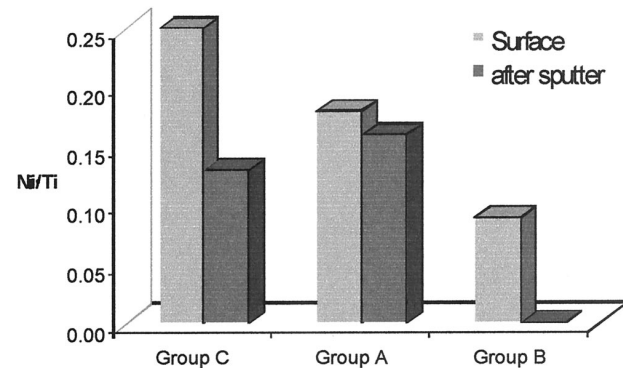


FIG 2. Plot of the atomic nickel/titanium on the surface of instruments of groups A, B, and C. Group A: Ni/Ti ratio = 0.17, group B: Ni/Ti ratio = 0.1, group C: Ni/Ti ratio = 0.25.

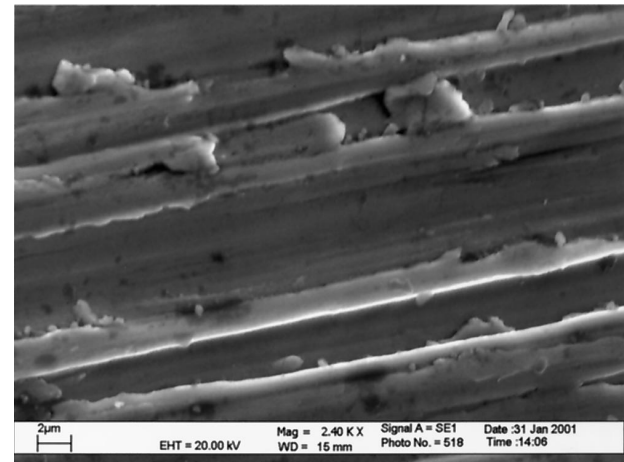


FIG 3. Surface of GT Rotary size 20 0.6 taper of Group C. Typical longitudinal features of NiTi instruments. Original magnification  $2400 \times$ .

the others two groups. In this case the longitudinal features, which are evident in new instruments, were not present (Fig. 5). Grains of approximately 100 nm constituted the deposited layers (Fig. 6). A few large grains of approximately  $1 \mu\text{m}$  are visible in the microphotograph.

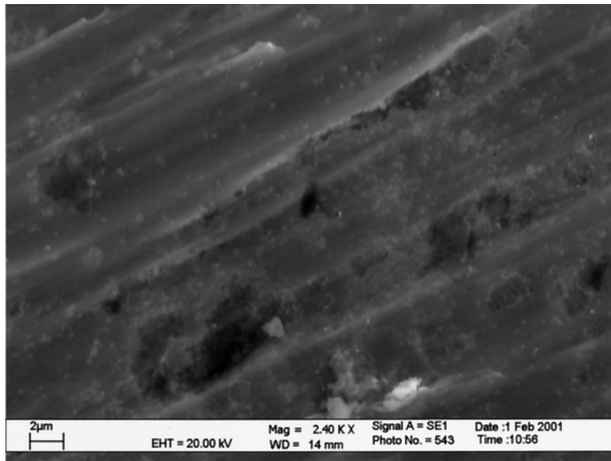


FIG 4. Surface of GT Rotary size 20 0.6 taper of Group A. The surface appears covered by layers of deposited materials with few crystalline grains. The surface of instrument appears more homogeneous and smooth. Original magnification 2400  $\times$ .

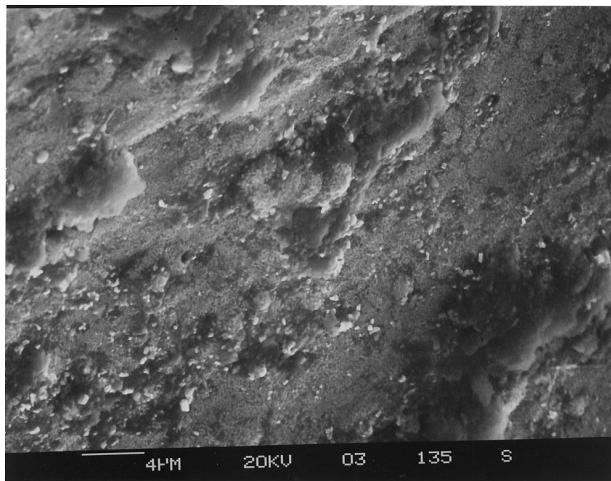


FIG 5. Surface of GT Rotary size 20 0.6 taper of Group B. The surface appears covered by layers of deposited materials with the presence of small grains. Original magnification 2400  $\times$ .

## DISCUSSION

XPS analysis shows a different in-depth concentration of nitrogen among samples from groups A, B and C. This observation indicates that the nitrogen-rich layers have a different thickness. In the case of group B the nitrogen/titanium ratio is approximately 1 after sputter, thus showing that the layers under the surface are also nitrogen-rich. This ratio suggests that the deposited material is TiN. This layer of titanium nitride created on the surface of the instrument can increase the cutting efficiency and wear resistance in that the instrument becomes harder on the surface and thus more effective in its shaping ability (10).

The SEM observations show that the deposition processes change the surface morphology. The nitrogen-containing film deposited on the instruments of group A is not constituted by well-defined crystalline grains, but mainly by continuous layers. This morphology suggests the presence of amorphous materials with a poor crystalline structure. Samples from group B show a deposited

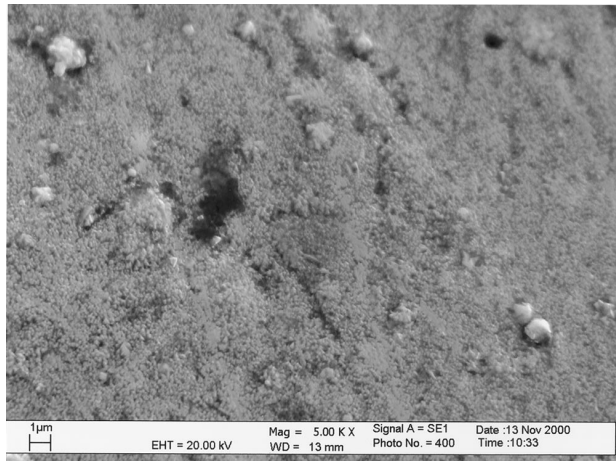


FIG 6. Presence of grains of 100 nm size on the surface of a sample of Group B. Original magnification 5000  $\times$ .

film composed of well-defined grains. This different morphology can be an indication of the presence of TiN film with a crystalline structure.

Finally, XPS analysis seems to confirm that the nitrogen deposition process moves the nickel element from the surface towards the bulk. Note that the lower amount of Ni on the surface was found in the samples from group B. This effect of the PVD process can be of interest for NiTi biomedical application.

MOCVD and PVD processes have been proved able to fabricate hard coating on NiTi instruments. However, further studies are underway to optimize the process conditions to obtain hard coatings of various thicknesses and compositions. Moreover, studies are needed to evaluate the possible increase in resistance to wear and the cutting ability of instruments covered by these hard coatings.

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