ASSESSMENT OF THE EFFECT OF THE IONIC IMPLANTATION BY PLASMA IMMERSION ON THE FLEXIBILITY OF THE NICKEL-TITANIUM ENDODONTIC FILES

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Abstract*. Due to its pseudo elastic behavior, the nickel-titanium (nitinol) alloy has been used in the manufacture of endodontic instruments in recent years, being especially useful for curved canals preparation. Extensive research has been carried out to improve the wear resistance of the nitinol instruments without create modifications in the bulk of the files. The purpose of this work was to measure the flexibility of commercially available type K stainless steel and nickel-titanium endodontic files, submit the nitinol files to plasma immersion ion implantation and assess the treatment effects on the same property. The instruments flexibility was measured throughout the bending moment test at 30^o and 45^o according to the American Dental Association specification n^o 28. The hardness of the files was measured before and after treatment by the Vickers method. The instruments surface state was observed throughout scanning electronic microscopy and the surface chemical composition of treated instruments was determined throughout the X-Rays photoelectron spectroscopy. The results found have led to the conclusion that no statistically significant change on the instruments flexibility was observed after the plasma immersion ion implantation.*

Key-words*: endodontic files, nickel-titanium, ionic implantation.*

1. Introduction

The properties of shape memory, pseudoelasticity and biocompatibility found on the equiatomic nickel-titanium alloy are the major reasons for its growing utilization as biomaterial. When this alloy is deformed beyond a certain level of force, its austenitic structure becomes instable and changes to the so-called stress induced martensite. If the force is released, a structure reversion takes place and the body original shape is resumed. Due to the fact that the nitinol can be submitted to a larger degree of strain in comparison with the majority of the engineering metals, its behavior is called superelastic or pseudoelastic (Ford and White, 1995; Reis and Elias; 2001).

The initial application of the nitinol alloy in endodontics is due to Walia, Brantley and Gerstein (1988) who, from an orthodontic wire of dia. 0.5 mm, machined the first Ni-Ti endodontic file. Given its superior ductility, the nickel-titanium files are especially suitable for the instrumentation of curved root canals replacing the formerly employed stainless steel files. Endodontic files are used in the root canals treatment to promote mechanical cleanliness in association with chemical solutions and to shape the tooth canal in a continuous tapered format (Moysés *et al.*, 2001). Due to its super-elasticity the nickel-titanium files must be manufactured by machining rather than by torsion. Experimental studies have been carried out with the purpose of improving the tribological properties of the nitinol instruments surface (Lee *et al.*, 1996; Rapisarda *et al.*, 2000; Tripi *et al.*, 2002), thus increasing the dentin cutting capacity without reducing the bulk ductility. The description of studies using the treatments of boron and nitrogen ions implantation, thermal nitriding, reaction of the wet NH_3 with Ni-Ti under high temperatures (300^{o}C) and metal organic chemical vapor deposition (MOCVD) using Ti $(Et_2N)_4$ as titanium and nitrogen precursor is available in a number of technical papers, however, no mentions are made on the effect of such treatments on the instruments flexibility. The ionic implantation is defined as the modification of the solids subsurface by means of ions with high kinetic energy from a plasma surrounding the material surface or from an ion gun.

Based on the above facts, the purpose of this study is to determine the flexibility of commercially available stainless steel and nitinol files, submit the nickel-titanium instruments to the plasma immersion ion implantation process, and assess the effects of such treatment on this same mechanical property.

2. Material and methods

2.1. Materials

Endodontic hand files manufactured by Maileffer – Switzerland, type K, size ISO 35, length 25 mm made of stainless steel (commercially named Flexofile) and nickel-titanium (commercially named Nitiflex) were employed in this study. None of the instruments was autoclaved or submitted to sterilization previously to the testing.

2.2. Methods

Vickers microhardness measurements, scanning electronic microscopy (SEM) and flexibility tests were carried out for the stainless steel file in the as-received condition and before and after treatment for the nitinol instruments. The X-Rays photoelectron spectroscopy for the nitinol files was carried out after the surface treatment.

2.2.1. Vickers Microhardness

The Vickers microhardness was measured in a equipment model FM-300-E, made by Future-Tech-Japan. The hardness indentations were made on the files core, along the length of the cutting shaft, on six equi-spaced points, under a load of 300 g and a residence time of 15 s. Two samples of each file condition were tested (two samples of SS files, two samples of Ni-Ti files before treatment and two samples of Ni-Ti files after treatment).

2.2.2. Scanning Electronic Microscopy

An equipment Leo 1450V was used for the scanning electronic microscopy. The images were taken in retro-scattered mode on the midway of the cutting length (region of the D8 diameter) under magnification 250X and 1000X.

2.2.3. Flexibility Tests

The files flexibility was expressed by the bending moment at 30^o and 45^o. Five samples of each file condition were tested (five samples of SS files, five samples of Ni-Ti files before treatment and five samples of Ni-Ti files after treatment). The tests were carried out in a meter (Fig. 1) designed and made according to the requirements of the A.D.A. specification # 28. The test methodology comprised the following steps: a) file handle removed on the point of attachment to the instrument shaft; b) file clamped perpendicular to the axis of the clamping device at a point 3 mm from its tip; c) approach the file shaft to the fixed stop located at 17 mm from the file tip; d) manual application of an increasing load on the tip of the instrument to bend the file shaft. The reaction force to this load application was then read in a Mettler digital scale, model PB 3002, accuracy of 0.0010 g, on which the fixed spot was set. At the same time, this normal force was transferred, by means of a rack and pinion mechanism, to a shaft with a pointer that spinning on a bevel protractor allowed the reading of the bending angle.

Figure 1 – Bending moment meter

2.2.4. X-ray Photoelectron Spectroscopy

This method was employed to determine the nitinol files surface chemical composition after treatment. The X – Rays photoelectrons spectra of the samples were obtained with a hemispheric analyzer HA 100 VSW operated in transmission mode with an energy of 44 eV and keeping a maximum pressure of 2×10^{-8} mbar between measurements.

2.2.5. Surface Treatment

Prior to the treatment, the file handle was removed and the shaft submitted to ultrasonic cleaning in three stages of ten minutes each (first in trichloroethylene; then in acetone and finally in isopropyl alcohol). At the end of the cleaning process, the file shaft was stored in a closed container with isopropyl alcohol, from where it was transferred to the sample holder inside of the reactor at the beginning of the surface treatment.

The plasma immersion implantation process comprised the following steps:

a) Reactor was closed and vacuum established (10^{-6} Torr reached in 60 minutes);
b) A potential difference of (– 1000 V) is applied on the file shaft and hydrogen h.p. (99.999%) is admitted inside of the reactor with the vacuum pressure dropping to 10^{-2} Torr. Plasma was formed under such conditions and kept for 120 s to complete the file shaft surface cleanliness;
c) The negative pulsed DC source is turned off and plasma formation is interrupted;
d) The vacuum is formed again as described on item (a) above;
e) Nitrogen h.p. (99.999%) pumped to the inside of the reactor up to an working pressure of 35 – 45 Torr;
f) File shaft is submitted to a second polarization of (– 1000 V), forming the plasma of nitrogen;
g) File was kept under immersion for 1 h, with the plasma current monitored to assure that the temperature inside of the reactor would not raise above 300^{o}C (controlled by type “k” thermocouple);
h) Energy source turned off and nitrogen pumping interrupted.
i) Reactor opened and file removed for the after-treatment testing.

2.2.6. Statistical Methods

The one-way ANOVA followed by the Tuckey comparison test were used to compare hardness and flexibility of the different test groups. A significance level of 0.05 was adopted for the study.

3. Results

3.1. Vickers microhardness

The results of the endodontic files microhardness are shown at Tab. 1.

Table 1 – Endodontic files Vickers microhardness

Endodontic File	Location on the cutting length						Mean	Standard Deviation
	D_2	D_4	D_6	D_8	D_{10}	D_{12}		
Flexofile	559.3	548.4	567.2	536.6	556.2	558.2	554.4	1.9
Nitiflex (as-received)	373.7	377.5	374.0	378.6	380.8	367.7	375.2	6.6
Nitiflex (after treatment)	376.3	360.2	360.8	362.2	361.3	356.4	362.9	7.6

3.2. Bending moment

The results of the endodontic files bending moment are shown at Tab. 2.

Table 2 – Endodontic files bending moment

Bending Angle (degrees)	Bending Moment (g.cm)						
	Flexofile		Nitiflex (as-received)		Nitiflex (after treatment)		A.D.A. spec #28
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	
30	67.8	4.0	23.7	2.2	20.1	2.1	104.4 Max
45	77.7	2.8	26.9	2.3	25.5	2.9	129.6 Max

3.3. Scanning Electronic Microscopy

The SEM images have revealed the distinct file manufacturing processes of torsion and machining followed by polishing respectively to the stainless steel and nitinol instruments. Neither the effects of the surface treatment nor the effects of the bending test are perceived on the nitinol files surfaces. The amount of porosities in the nitinol files is considerably higher than in the steel files.

3.4. X-ray Photoelectron Spectroscopy

The spectra for the elements Titanium, Nitrogen and Nickel are shown at Fig. 2a/b/c, respectively.

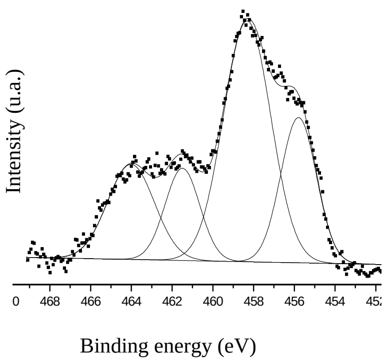

Figure 2a – Spectrum for the element Titanium

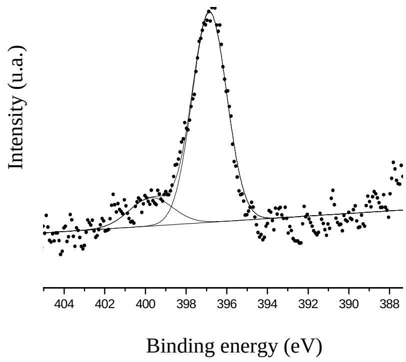

Figure 2b – Spectrum for the element Nitrogen

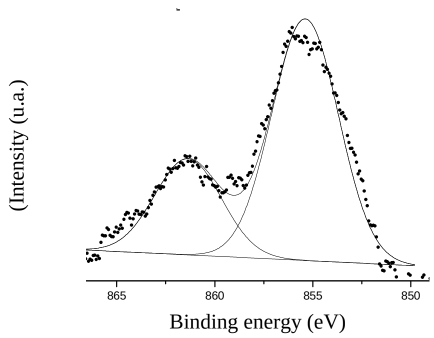

Figure 2c – Spectrum for the element nickel

Based on the above charts, the surface treatment promoted a Ni:Ti atomic ratio of 0.23 and a N:Ti atomic ratio of 1.15 on the nickel-titanium instruments.

4. Discussion

4.1. Vickers microhardness

The hardness results of both, nitinol and steel files, in the as-received condition are very similar to the findings of Blockhurst & Denholm (1996), Silva (2001) and Amaral (2002). The stainless steel files hardness is significantly higher (p « 0.001) than the hardness of the nitinol files. The hardness values found for the treated nitinol files were significantly lower (p « 0.001) than the hardness values measured before the implantation process, however no practical undesirable effect was perceived on the instruments flexibility. The purpose of monitoring the nitinol files core hardness after the surface treatment was to measure the effect of treatment time and temperature on this property, and prevent the hardness reduction as reported by Kuhn, Tavernier e Jordan (2001).

4.2. Bending moment

The values found for the files bending moment at 30º and 45º met the requirements of the American Dental Association specification # 28 (Council on Dental Materials and Devices, 1976). The flexibility of the stainless steel files was significantly lower (p «0.001) than the nitinol files, in agreement with previous findings of Canalda-Sahli, Brau-Aguadé and Berastégui-Jimeno (1996), Camps, Pertot and Levallois (1995), Haïkel *et al.*(1998) and Kazemi, Stenmann and Spångberg (2000).

Statistical evidences that the ionic implantation process has changed the flexibility of the nitinol files have not been found (p = 0.09 for the testing at 30º and p = 0,41 for the testing at 45º), as predicted by Rapisarda *et al.* (2001), therefore the improvement in the instrument cutting efficiency by the implantation process, without jeopardizing the ductility of the instruments, can be expected. It is also worth to mention that the steel files have shown permanent deformation after the bending testing at 45º, fact not observed for the nitinol files in agreement with the finding previously reported by Camps and Pertot (1995).

4.3. Surface Treatment

The major advantages of the Plasma immersion ion implantation process over other conventional options, such as the ion bean implantation process or thermal nitriding are:

- Temperature of treatment does not change the material structure, shape and dimensions;
- More cost-efficient and less complex in comparison with the Ion bean implantation process
- All plasma ions (monatomic or molecular) are implanted.
- No case formation since that only the material sub-surface properties are improved;
- Low energy consumption
- Few process materials required;
- Process is clean (vacuum) and environmentally-friend;
- Low cost equipment;
- No restrictions to the treatment of complex shapes as the sheath conformably surrounds the surface and all the surfaces are implanted at the same time (Le Couer *et al.*; 2000).

In this study our option was to promote the plasma with nitrogen (N_2 e N) ions to create compression tension and hard inclusions (normally nitrides) finely dispersed on the material surface, thus contributing to higher wear resistance.

Due to the surface heterogeneity the wear of implanted materials is non-uniform, usually being discrete in the beginning of the friction work and increasing with the continuity of the applications. The implantation process dramatically changes the material properties, however only in a surface depth of few nanometers.

In addition of increase the material surface mechanical properties, the good biocompatibility of the titanium nitride is a key factor to encourage its application on surgical and dentistry instruments (Burakowski & Wierzchón, 1999).

4.4. Scanning Electronic Microscopy

The SEM images of the file surfaces neither reveal any morphological change due to the surface treatment nor due to the bending moment test. This finding is in agreement with similar conclusion drawn by Rapisarda *et al.* (2001), and can be explained by the diffuse structural change on the material sub-surface rather than a material hardened case formation (Burakowski and Wierzchón, 1999).

4.5. X-ray Photoelectron Spectroscopy

Table 3 shows the atomic ratios of Ni:Ti and N:Ti from a number of surface hardening processes.

Table 3 - Ni:Ti e N:Ti Atomic Ratios

Treatment	Group		Reference	Atomic Ratio	
	Experimental	Control		Ni:Ti	N:Ti
Plasma Immersion Íon Implantation	x		This study	0.23	1.15
Ion Bean Implantation	x		Rapisarda *et al.*, 2000	0.50	1.20
Thermal Nitriding	x		Rapisarda *et al.*, 2000	0.30	0.50
NH_3 Deposition	x		Tripi *et al.*, 2002	0.25	0.90
MOCVD	x		Tripi *et al.*, 2002	0.18	2.00
None		x	Tripi *et al.*, 2002	0.30	0.20
None		x	Rapisarda *et al.*, 2000	0.20	<0.10

The X-ray Photoelectron Spectroscopy has confirmed the formation of Titanium Nitride from the application of the ionic implantation process. The contribution of the titanium nitride towards the improvement of the nitinol files wear resistance has already been proved by Rapisarda *et al.* (2000) and according to Tripi *et al.* (2002), it can also prevents the possible oxidation of the outer layers of the instruments during the autoclave (sterilization) processes.

As shown at Tab. 3, the N:Ti atomic ratio obtained with the plasma immersion implantation process was higher than the ones achieved in conventional processes and comparable with the ratio obtained with the ion beam implantation process, that is more complex and less cost-efficient (Rapisarda *et al*, 2000).

Tripi *et al* (2002) has suggested that the process of nitrogen deposition moves the Nickel element from the surface towards the bulk of the instrument and a similar trend was observed in the present study.

5. Conclusion

Based on the results above described, it can be concluded that the application of the plasma immersion íon implantation process has not significantly (p « 0.001) affected the flexibility of the nitinol instruments.

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