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Wear resistance of nickel–titanium endodontic files after surface treatment

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Abstract *Objectives* The purpose of this work was to submit the Nitinol files to plasma immersion ion implantation (PIII) and evaluate the effects of the surface treatment. *Materials and Methods* Wear resistance was determined in vitro by using an equipment for the application of horizontal movements on previously prepared notched plates made of resin. Vickers microhardness was measured in plates and files, before and after surface treatment and the surface chemical composition of the instruments was determined by X-rays photoelectron spectroscopy. *Results* The hardness values found for the treated Nitinol files were significantly lower than the hardness values measured before the implantation process. The comparison of commercially available instruments shows that the wear resistance of the stainless steel file is higher than the resistance of the Nitinol. *Conclusions* The results found led to the conclusion that the surface treatment significantly increased the Nitinol files wear resistance.

1 Introduction

The properties of shape memory, pseudoelasticity and biocompatibility found on the equiatomic nickel–titanium alloy have been 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 [1].

The initial application of the Nitinol alloy in endodontic is due to Walia, Brantley e Gerstein [2] who, from an orthodontic wire of diameter 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. Due to its super-elasticity the nickel–titanium files must be manufactured by machining rather than by torsion.

The ionic implantation is defined as the modification of the solids subsurface by means of ions with high kinetic energy from plasma surrounding the material surface or from an ion gun. Experimental studies have been carried out with the purpose of improving the tribological properties of the Nitinol instruments surface [3–6], 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°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. Based on the above

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facts, the purpose of this study is to measure the wear resistance 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 this same mechanical property.

2 Material and methods

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

2.1 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: Reactor was closed and vacuum established (10^{-6} Torr reached in 60 min); a potential difference of (−1,000 V) was applied on the file shaft and hydrogen h.p. (99.999%) 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; the negative pulsed DC source was turned off and plasma formation interrupted; the vacuum was formed again as described on item (a) above; nitrogen h.p. (99.999%) pumped to the inside of the reactor up to an working pressure of 35–45 Torr; file shaft submitted to a second polarization of (−1,000 V), forming the plasma of nitrogen; 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°C (controlled by type "k" thermocouple); energy source turned off and nitrogen pumping interrupted; reactor opened and file removed for the after-treatment testing.

2.2 Vickers microhardness

Vickers microhardness was measured in an equipment model FM-300-E (Future-Tech-Japan). Two samples of each file condition were tested for hardness, on the file core and 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.

2.3 Wear testing

To minimize the operator influence on the test results, the wear resistance was determined in vitro by using the electric powered device, shown at Fig. 1a, designed for the application of filing horizontal movements on previously prepared notched plates (Fig. 1b). Plates were made of phenolic thermosetting resin under controlled conditions, with the dimensions of 3 mm of thickness by 20 mm width by 30 mm length and four equi-spaced notches of 0.6 mm of width by 1 mm by height per plate side. In previous study, Vickers hardness of the plates was compared with measurements made on bovine femur bone and found statistically similar (*P* value: 0.886). Wear plates hardness measurements were taken between the plate notches under a load of 500 g and a time of 15 s.

The wear cycle key parameters were the following: filling frequency corresponding to 138 cycles/min; wear time of 5 min per notch; 4 notches per file; 5 files per condition; cutting shaft utilized range was D_0–D_{13}; irrigation with 2.5 cc of physiological solution; load of 150 g vertically applied on the file. The file wear resistance was

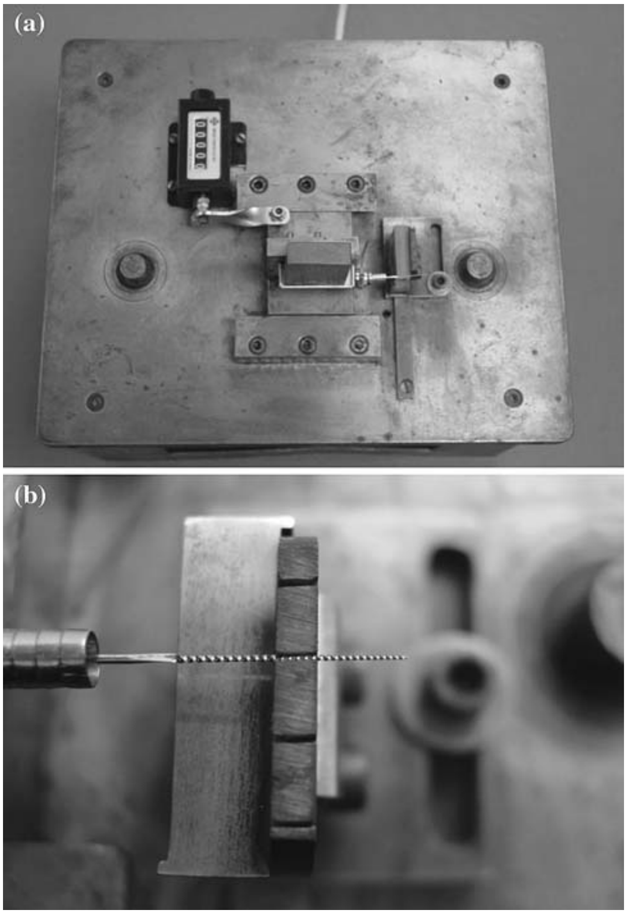

Fig. 1 (**a**) Wear test equipment; (**b**) reciprocating horizontal movements on the resin notched plate

expressed as the notched plate weight loss (g) in dry basis per filling cycle.

2.4 X-rays photoelectron spectroscopy (XPS)

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.

2.5 Statistical methods

The one-way ANOVA, followed by the Tukey comparison test, was used to compare the wear resistance and hardness of the different groups. A significance level of 5% was adopted for the study.

3 Results and discussion

Tripi et al. [6] have 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.

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 [7].

In this study our option was to promote the plasma with nitrogen (N_2 and 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 increasing 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 [8].

3.1 Vickers microhardness

The results of the endodontic files microhardness are shown at Table 1. The hardness results of both, Nitinol and stainless steel files, in the as-received condition are very similar to the findings of Blockhurst and Denholm [9]. The stainless steel files hardness was significantly higher ($P \ll 0.001$) than the hardness of the Nitinol files. The hardness values found for the treated Nitinol files were significantly lower ($P \ll 0.001$) 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 [10].

3.2 Wear resistance

The results of the endodontic files wear resistance are shown at Table 2. The equipment used for the wear test was designed to reduce, at the possible extent, the influence of the operator on the test results. To meet this intent, and in line with the methodology formerly adopted by other researchers [10, 11], the test machine was provided of resources to assure the required repeatability and accuracy of the number of cycles, the frequency and range of the filling movement, the load on the file and the proper placement of the wear plate in the holder at the test machine. The wear plates were molded in uniform conditions and key dimensions controlled with a steel gage. The most important wear cycle parameters, such as the load on

Table 1 Endodontic files Vickers microhardness

Endodontic file	Location on the cutting length						Mean	S.D.
	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	11.9
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

Table 2 Wear resistance of the endodontic files

File type	Parameter	Weigh loss per notch (g × 10^{-4})			
		Notch # 1	Notch # 2	Notch # 3 and 4	Total
Flexofile	Mean	49.2	31.4	26.8	107.4
	S.D.	3.9	1.8	2.3	5.8
	% Over total	45.8	29.2	25.0	(100.0)
Nitiflex (as-received)	Mean	35.8	25.8	32.4	94.0
	S.D.	3.7	2.6	3.0	5.8
	% Over total	38.1	27.4	34.5	(100.0)
Nitiflex (after treatment)	Mean	51.0	42.2	33.4	126.6
	S.D.	3.9	3.0	2.7	8.6
	% Over total	40.3	33.3	26.4	(100.0)

the file (150 g) and the frequency of the reciprocating movement (138 rpm) were set to the same values used in a previous work. The irrigation during the filing cycle was used with the purpose of reducing the friction between the instrument and the wear plate and preventing the accumulation of debris on the file cutting edge. The usage of a number of irrigation agents, such as the sodium hypochlorite, deionized water and physiological solution, have already been reported, but none of them seem to play a important role on the cutting efficiency of the endodontic instrument [12, 13]. For this reason, at this study, the physiological solution was used as irrigation agent.

A significant difference on wear resistance was revealed from the results obtained. The comparison of commercially available instruments shows that the wear resistance of the stainless steel file is higher than the resistance of the Nitinol files in agreement with previous findings of Zuolo and Walton [14] and in opposition with the results of Camps and Pertot [15]. After ion implantation, the highest wear resistance and the most negligible effect of the filling cycle on the instrument cutting edge was found for the Ni–Ti file confirming previous results of Rapisarda et al. [4, 5].

Table 3 Ni:Ti and N:Ti Atomic ratios

Atomic ratios	Ni:Ti	N:Ti
Actual results	0.23	1.15

Table 4 Atomic ratios for the Nitinol files after surface treatment

Treatment	Groups		Reference	Atomic ratio	
	Experimental	Control		Ni:Ti	N:Ti
PIII	×		This study	0.23	1.15
Ion Bean Implantation	×		[4]	0.50	1.20
Thermal Nitriding	×		[4]	0.30	0.50
NH_3 Deposition	×		[6]	0.25	0.90
MOCVD	×		[6]	0.18	2.00
None		×	[6]	0.30	0.20
None		×	[4]	0.20	<0.10

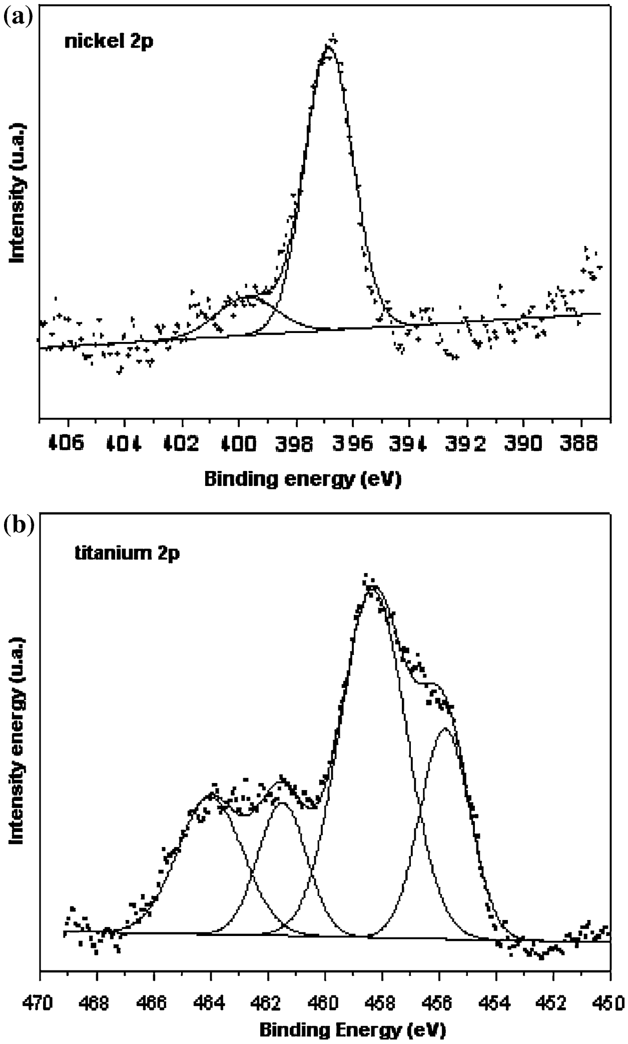

Fig. 2 XPS spectra: (**a**) nickel; (**b**) titanium

3.3 X-rays photoelectron spectroscopy

The atomic ratios found for the nickel–titanium instruments, after the surface treatment, are shown at Table 3. The atomic ratios of Ni:Ti and N:Ti from a number of surface hardening processes are shown at Table 4.

The XPS has confirmed the formation of titanium nitride from the application of the ionic implantation process (Fig. 2). The contribution of the titanium nitride towards the improvement of the Nitinol files wear resistance has already been proved by Rapisarda et al. [4] and, according to Tripi et al. [6], it can also prevents the possible oxidation of the outer layers of the instruments during the autoclave (sterilization) processes.

As shown at Table 4, 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 [4].

4 Conclusions

Based on the above-described results, it can be concluded that the application of the plasma immersion ion implantation process has significantly ($P \ll 0.001$) increased the Nitinol files wear resistance.

The implantation process reduced the hardness of the Nitinol files, however, no practical undesirable effect was perceived on the instruments flexibility.

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