SEM Observations and Differential Scanning Calorimetric Studies of New and Sterilized Nickel-Titanium Rotary Endodontic Instruments

Georgia B. Alexandrou, Konstantinos Chrissafis,† Leonidas P. Vasiliadis,* Eleni Pavlidou,† and E.K. Polychroniadis†*

Abstract

Scanning electron microscopy (SEM) and differential scanning calorimetric (DSC) studies were utilized to investigate surface and microstructure of two brands of rotary nickel-titanium (NiTi) endodontic instruments, in the as-received condition and after subjection to 1, 6, and 11 sterilization cycles. A total of 66 ProFile ($n = 33$) and Flexmaster ($n = 33$) files were examined. SEM observations indicated the presence of surface imperfections and adherent material in all new and sterilized instruments and an increase in surface roughness of the instruments that underwent multiple sterilizations. DSC measurements showed that the specimens of both brands, in the as-received condition and after 11 sterilizations, were completely austenite in the oral environment temperature, suggesting that they are capable of superelastic behavior in appropriate clinical conditions. *(J Endod 2006;32:675–679)*

Key Words

DSC, Flexmaster, Nickel-titanium endodontic instruments, ProFile, sterilization

From the *Department of Endodontology, Dental School, †Physics Department, Solid State Physics Section, Aristotle University of Thessaloniki, Thessaloniki, Greece.

Address requests for reprint to Asst. Prof. Leonidas P. Vasiliadis, Department of Endodontology, Dental School, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece. E-mail address: vl@dent.auth.gr.

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Nickel-titanium (NiTi) endodontic files are particularly helpful for successful shaping of curved root canals, demonstrating greater flexibility and superior resistance in bending and torsion compared with stainless steel instruments (1–3). Endodontic instruments are frequently re-used, imposing strictly their sterilization between uses. The effect of sterilization procedures on physical and mechanical properties of the NiTi files has not yet been adequately evaluated. Some authors reported that heat sterilization increase number of rotations-to-breakage of NiTi instruments (2, 4), while others showed that had no consistent or significant effect (5–8). Some researchers (9, 10) found that heat sterilization leads to reduction of cutting efficiency of the NiTi files.

The NiTi alloys for endodontic instruments, which are based upon nearly equiatomic intermetallic compound NiTi (11), were originally introduced for orthodontics (1, 12–14). They have the inherent ability to undergo phase transformation within NiTi matrix, from austenite (parent phase) to martensite (daughter phase) with application of temperature or stress, giving rise to shape memory effect (SME) and superelasticity (SE). When the alloy is cooled through a critical transformation temperature range (TTR), change in crystal structure occurs, known as temperature-induced martensitic transformation. This deformation can be reversed to its original parent (austenitic) phase, by heating the alloy above TTR (shape memory effect). In case of stress-induced martensitic transformation, austenite transforms to martensitic NiTi as a function of application of stress, reverting back to austenite when unloaded (superelasticity).

Phase transformations are associated with significant changes in mechanical properties of the alloy, thus structure of the NiTi alloy is central to the clinical performance of the instruments. Differential Scanning Calorimetry (DSC) has been successfully used to investigate phase transformation within NiTi matrix of popular brands of endodontic instruments (15-18). Transformations are revealed as endothermic peaks on the heating DSC curves and as exothermic peaks on the cooling DSC curves, indicating which phase of the NiTi alloy exists at a given temperature.

The purpose of this study was to investigate surface and microstructure of two popular brands of NiTi rotary endodontic instruments, in the as-received condition and after multiple sterilization cycles under dry heat sterilizer, using Scanning Electron Microscopy (SEM) and DSC.

Materials and Methods

A total of 66 new rotary NiTi endodontic instruments, taper 0.04, size 30 and 25-mm long were examined: 33 ProFile (Densply/Maillefer, Ballaigues, Switzerland; Lot. 5149890) and 33 Flexmaster (Endodontic Synergy, VDW, Munich, Germany; Lot. 0409310298) files. The sterilizations were conducted in dry heat sterilizer (Technomedica, Milano, Italy), at 180°C for 120 min.

SEM

Twenty-seven files of each brand were examined in a type JSM840A (JEOL, Tokyo, Japan) Scanning Electron Microscope, after they were divided into three groups.

The first group included three ProFile and three Flexmaster instruments for surface observations in the as-received condition and after subjection to 11 sterilization cycles.

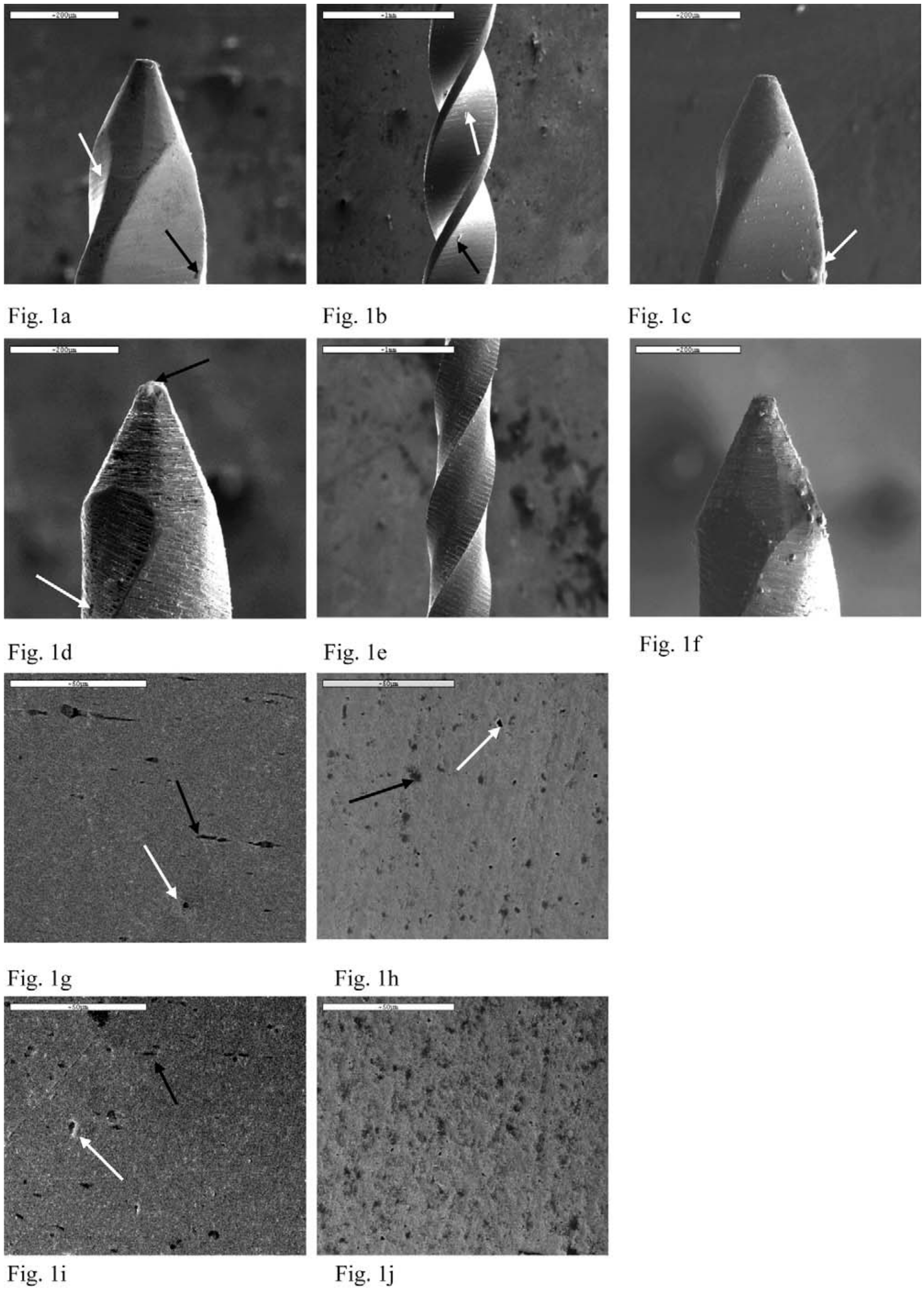

Figure 1. (a) Flattened, non cutting tip, with few metal stripes (white arrow) and pits (black arrow) of a ProFile instrument in the as-received condition. Surface roughness is considered minimal (level 1). Original magnification: 200×. (b) Active part of an as-received ProFile instrument (with distinct radial lands). Metal stripes (white arrow) and adhered material (black arrow) are distributed along the surface of the file. Original magnification: 75×. (c) ProFile specimen that was subjected to 11 sterilization cycles. Debris remained (white arrow), while surface roughness is clearly increased (level 3). Original magnification: 75×. (d) Flexmaster instrument in the "as-received" condition with flattened, noncutting tip, excessive metal stripes, debris (black arrow) and pitting (white arrow). Moderate roughness of the surface (level 2) is evident. Original magnification: 200×. (e) Distinct metal stripes along the length of a Flexmaster file in the as-received condition (without radial lands). Original magnification: 75×. (f) Flexmaster sample after 11 sterilizations. Increased surface roughness (level 3), remained debris and surface irregularities are detected. Original magnification: 200×. (g) Longitudinal section of a ProFile file in the as-received condition. Holes (white arrow) and inclusions (black arrow) in the NiTi matrix are observed. Minimal presence of surface roughness (level 1). Original magnification: 1000×. (h) Cross-section of an as-received Flexmaster specimen. Holes (white arrow) and inclusions (black arrow) are clearly detected. Surface roughness is considered minimal (level 1). Original magnification: 1000×. (i) Longitudinal section of an 11 times sterilized ProFile instrument. Increased surfaced roughness (level 3), holes (white arrow) and inclusions (black arrow) are shown. Original magnification: 1000×. (j) Cross-sectioned surface of a Flexmaster sample that was sterilized 11 times. Holes, inclusions and increased surface roughness (level 3) are observed. Original magnification: 1000×.

In second and third groups of analysis, 12 instruments of each brand were cross-sectioned and another 12 instruments were longitudinally sectioned and then examined in subgroups of 3, after 0, 1, 6, and 11 sterilizations. For cross and longitudinal sections, samples were embedded in epoxy resin and after wet grinding with SiC papers, they were polished with diamond powder down to 1 μm in a grinding polishing machine (Struers A/S, Ballerup, Denmark).

All specimens were cleaned in an ultrasonic water bath for 15 min before sterilization procedure. Finally, they were vacuum-coated with a thin layer of conductive carbon and studied under SEM.

The level of surface roughness of the specimens was rated and scored on four appearances, using a predefined scale and selected SEM pictures:

Level 0 = absence of roughness,

1 = minimal roughness,

2 = moderate roughness and

3 = increased roughness.

DSC

Six instruments of each brand were examined: three in the as-received condition and other three after 11 sterilizations.

The DSC measurements were conducted with a DSC 141 device (Setaram, Lyon, France), using a liquid nitrogen cooling accessory (Setaram) to achieve sub-ambient temperatures. During the measurements the DSC cell was purged with dry nitrogen. The linear heating or cooling rate was 10°C/min. For each analysis, the specimen was first cooled from room temperature to −130°C, then heated to 150°C to obtain the heating DSC curve and subsequently cooled from 150 back to −130°C for DSC cooling curve. To test reproducibility of the measurements, the same heating–cooling cycle was repeated a further two times. Test specimens were carefully sectioned with a water-cooled, slow-speed diamond saw to minimize mechanical stresses that might change the proportions of the austenitic and the martensitic NiTi. Each test specimen (12 mgr in weight) consisted of three segments of the file, each 4 to 5 mm in length. Specimens were placed in an aluminum crucible, while an empty aluminum crucible was used as reference.

The data were analyzed as a 2 × 2 factorial in a completely randomized design with three replications. Comparison of means was made at the 0.05% level of significance.

Results

SEM Observation

Debris, metal stripes, pitting, and milling marks were detected on surface of all as-received specimens. Morphometric variations occurred, even among instruments of the same brand. New ProFile instruments with sharpened or flattened tips, wider or thinner radial lands, and surface imperfections were observed (Fig. 1*a*, *b*). After the 11 sterilization cycles, debris remained while surface roughness was increased from level 1 to 3 (Fig. 1*c*).

SEM observations were similar for the Flexmaster specimens. Dense metal stripes were the predominant finding (Fig. 1*d*, *e*). Increased surface roughness also occurred to multiple sterilized samples (Fig. 1*f*).

SEM observations of cross and longitudinal sections indicated the presence of inclusions and holes, randomly distributed in the matrix of the NiTi alloy, in all specimens of both brands (Fig. 1g, 1*h*). Increased roughness was observed in all samples that were exposed to repeated sterilizations (Fig. 1*b*, 1*h*).

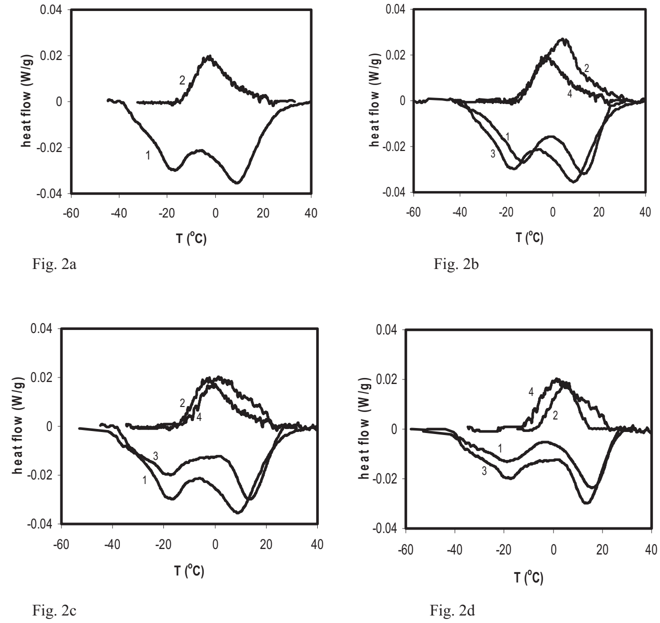

Figure 2. (a) DSC thermograph of an as-received Flexmaster specimen. 1: heating curve, 2: cooling curve. (b) DSC analyses of as-received specimens. 1: ProFile instrument—heating curve, 2: ProFile instrument—cooling curve, 3: Flexmaster instrument—heating curve, 4: Flexmaster instrument—cooling curve. (c) DSC plots of Flexmaster instruments. 1: as-received sample—heating curve, 2: as-received sample—cooling curve, 3: sample after eleven sterilization cycles—heating curve, 4: sample after eleven sterilization cycles—cooling curve. (d) DSC thermographs of samples subjected to eleven sterilization cycles. 1: ProFile specimen—heating curve, 2: ProFile specimen—cooling curve, 3: Flexmaster specimen—heating curve, 4: Flexmaster specimen—cooling curve.

DSC Measurements

Figure 2*a* shows characteristic DSC plot for an as-received Flexmaster specimen, after the subtraction of the baseline. DSC heating curve shows two-step endothermic transformation with overlapping peaks, which correspond to the initial transformation of martensite to an intermediate, R-phase at lower temperatures, followed by transformation of R-phase to austenite (A), at higher temperatures. At peak temperature of approximately 9°C, 50% of the austenitic phase is present (A_p temperature), while at approximately 34°C (austenite finish temperature- A_f) transformation to austenite is completed. The total enthalpy change (ΔH) for the overall transformation from martensitic to austenitic NiTi phase was approximately 8.3 J/g. DSC exothermic, cooling curve shows one-step distinct transformation. The transformation product of this peak, correspond probably to the transformation from austenite to R-phase, whereas the transformation from R-phase to martensite at lower temperatures is difficult to be identified (dissimulated in the baseline of the thermograph). The enthalpy during cooling was approximately 2.2 J/g. The thermographs of the as-received ProFile specimens are similar to thermographs of new Flexmaster specimens (Fig. 2*b*). The values that were obtained during their DSC measurements are reported in Table 1.

In Fig. 2*c*, *d*, heating and cooling curves of as-received and sterilized specimens of both brands are shown. The enthalpy changes and temperature values during DSC measurements of all specimens are summarized in Table 1. The ANOVA revealed significant differences between brands as well as between initial values and values after sterilizations. However, the effect of each factor is not the same at each level of the other factor. Thus, in case of A_f temperature, the mean value is

TABLE 1. Values determined from DSC analyses for new and sterilized ProFile and Flexmaster instruments

Properties	ProFile		Flexmaster		*$LSD_{0.05}$
	As-Received Samples	After 11 Sterilizations	As-Received Samples	After 11 Sterilizations	
Mean A_p (on heating)	13.4 °C	16.0 °C	8.9 °C	13.3 °C	0.8
Mean A_f (on heating)	31.1 °C	27.8 °C	33.9 °C	27.1 °C	0.9
Mean enthalpy change (ΔH) during heating	6.5 J/g	4.3 J/g	8.3 J/g	5.2 J/g	
Mean enthalpy change (ΔH) during cooling	4.2 J/g	1.3 J/g	2.2 J/g	2.4 J/g	

*LSD refers to least significant difference, which was set at 0.05%.

reduced after multiple sterilizations by 20% for the Flexmaster specimens, but only by 11% for the ProFile specimens.

Discussion

Manufacturing of NiTi endodontic files is more complex than that of stainless steel instruments. NiTi files, owing to superelasticity of NiTi alloy, have to be machined instead of twisted (11). However, grinding of NiTi alloy leads to surface imperfections, especially on the cutting edges of NiTi files. In the present study, the outer surface of all new rotary ProFile and Flexmaster instruments presented structural defects. The presence of the adherent material probably occurred from decomposition and oxidation of the lubricating oil used in machining the instruments (11, 19). The inclusions within NiTi matrix are presumed to be primarily titanium carbonitrides (20, 21), with a few NiTi oxides, which are formed during vacuum melting of NiTi alloy, while holes possibly originate during the wire-shaping process. Thermomechanical history of each file may also be responsible for the morphometric variations among the instruments of the same batch. Several authors reported also structural imperfections in new ProFile (19, 22) and Lightspeed (22–24) instruments.

The presence of surface irregularities on NiTi files may compromise their cutting efficiency (11, 25) and probably make them more prone to corrosion (2) and fracture (26). Thus, NiTi instruments, especially small sizes, should be used with caution (27–29). In contrast, Eggert et al. (24) supported that these surface irregularities are probably clinically insignificant. Some surface engineering techniques have been suggested to improve surface microhardness and corrosion resistance of NiTi instruments, that mainly involved ion implantation (10, 30–32).

In all samples that were subjected to repeated sterilizations, an increased surface roughness occurred compared to the un-sterilized samples. Possible explanation for this, might be alterations in thickness of the passive TiO_2 layer that covers NiTi surfaces, caused by repeated sterilization procedures (9, 33, 34). According to some authors, the increase in surface NiTi oxides leads to a decrease in cutting ability of NiTi instruments (9, 10).

From the temperature values (Table 1), significant differences are revealed between files of two brands and between new and sterilized instruments of the same brand. A_f values of the as-received instruments of both brands are higher than A_f values of sterilized files. However, A_f temperature values of all specimens are found smaller than the oral environment temperature (~37°C), meaning that the transformation from martensitic to austenitic NiTi is completed between room temperature (~25°C) and oral environment temperature. Because all specimens are completely austenite in the oral environment, these differences are not expected to have clinical impact. Superelasticity occurs when austenite is present, between A_s (austenite start) temperature and M_d temperature (above which stress-induced martensite can no longer be formed, about 25 to 50°C higher than A_f) (35), suggesting that all examined specimens of both brands are considered capable of superelastic behavior. These findings agree with previous observations on ProFile instruments (16, 17). Other studies found that ProFile instruments are completely austenite or a mixture of austenite and R-phase in the oral environment temperature (15, 18). For Flexmaster instruments no such previous information exists in literature.

All enthalpy values lie within the range that has been reported for some NiTi orthodontic wires (36). The enthalpy changes for the overall transformation from martensitic to austenitic NiTi in new Flexmaster instruments is higher (~8.3 J/g) compared with the values of new ProFile instruments (~6.5 J/g). According to Brantley et al. (16), it is tempting to speculate that this is possibly because of lower amounts of stable, work-hardened martensitic NiTi (which does not undergo transformation to austenitic NiTi) in the former instruments after manufacturing and might suggest a less advantageous microstructure for the ProFile files. This also may be plausible cause for the relatively lower values that were observed at samples that were subjected to eleven sterilizations in comparison with the as-received samples of the same brand. Thus, files that undergo multiple sterilizations might present a less advantageous microstructure.

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