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ORIGINAL ARTICLE

Surface and cross-sectional characterization of titanium-nitride coated nickel—titanium endodontic files

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Abstract *Background/purpose:* Although the effect of experimental surface modifications on various properties (e.g., fatigue, wear) on coated files have been tested in the past, there is no report for the coating quality of commercially available TiN coated files. The aim of this study was to characterize the surface and cross section of TiN coated endodontic files.
Materials and methods: TiN coated nickel—titanium endodontic files (EasyShape) were surface and cross-sectionally analyzed via scanning electron microscopy backscattered electron imaging and energy-dispersive X-ray spectroscopy analysis in spot, area, and line scan modes.
Results: Surface imaging revealed parallel oblong regions with higher mean atomic contrast, a finding attributed to increased Ni content. Cross-sectional analysis showed that the coating's average total thickness was 0.31 μm and consisted of a thin layered film. Energy-dispersive X-ray spectroscopy analysis revealed the presence of Ti, Ni, N, and O in the coating, whereas only Ni and Ti were identified in the bulk of the file. Ti and O showed their peak compositions at the bulk/coating and coating/surface interfaces, respectively, whereas N displayed a rather constant content within the coated region. The N and O contents started increasing inner to the coating/bulk interface, denoting possible diffusion of both elements to the subcoating region.

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Conclusion: Surface and bulk characterization showed no uncoated areas of the files tested. Apart from Ti, Ni, and N, oxygen was also identified within the coating region.

Introduction

Current technology may be used to apply a variety of surface treatments to modify the surface properties of dental devices and thereby improve their efficacy for a specific use. Specifically, titanium (Ti) nitriding and nitrogen (N) ion implantation have been experimentally tested since the 1980s in a variety of dental applications including orthodontic wires, implants, and abutments in order to increase surface hardness, electrochemical properties, abrasive/wear resistance, esthetics, and antimicrobial properties.[1]

In endodontics, producing files with a flexible core to easily follow root canal curvatures and a very hard surface to increase cutting efficiency is a promising concept for improving the efficacy of endodontic files. As a result, many experimental efforts have been exerted in the past to develop a hard coating on nickel—titanium (Ni—Ti) endodontic files. Ion implantation[2,3] and Ti nitride techniques using physical vapor deposition (PVD),[4–11] thermal nitriding,[7] and metal organic chemical vapor deposition[11,12] have been implemented to modify the surface properties of Ni—Ti endodontic files. The aforementioned studies reported the beneficial effect of surface treatment in cutting[9] and cleaning[5] efficacy, wear,[2,11,13] and corrosion resistance.[4,14] Both PVD and thermal nitriding have a positive effect on the fatigue life of endodontic rotary files,[6] but ion implantation has adversely affected fatigue resistance, possibly due to N diffusion within the grain boundaries of the alloy.[3] Specifically for the only commercially available rotary Ni—Ti system (EasyShape) with TiN coated files, it has been shown to retain the same shaping ability but with enhanced cleaning effectiveness compared to uncoated instruments.[5]

Despite the favorable reports, a few concerns have arisen over the quality and sustainability of PVD coated endodontic files following successive chemomechanical root canal preparations. Electrochemical findings showed that PVD coated files from the same manufacturer demonstrated a wide range of pitting potentials. This implies that the coating may not provide equal corrosion resistance to the whole surface of the endodontic file, and thus the coating method may need further standardization and/or optimization.[4] Studying the effect of autoclave sterilization *in vitro* without intermediate chemomechanical treatments in root canals, Spagnuolo et al[10] reported that roughness increased, whereas the N/Ti ratio decreased in files after 10 sterilization cycles compared to the as-received condition, implying morphological and elemental surface alterations.

Although the effect of various surface modifications have been studied in combination with selected properties (e.g., fatigue, wear, corrosion resistance), there is no published report on the quality of the coating itself. Therefore, the aim of this study was to characterize the surface and cross section of commercially available TiN coated endodontic files.

Materials and methods

A full kit of EasyShape System coated endodontic files [EasyShape (Lot: 822313); Komet Dental, Gebr. Brasseler GmbH & Co. KG, Lemgo, Germany] was received including successive sizes from #15 to #40. Figure 1 illustrates one coated file from this kit with the characteristic yellowish surface and a conventional uncoated Ni—Ti file for comparison purposes. The cutting surface of three as-received files (#15, #25, and #35) were analyzed using a scanning electron microscope (JSM 7600F; Jeol Ltd., Tokyo, Japan) coupled with energy-dispersive X-ray silicon drift detector (X-Max^N Oxford Instruments, Abingdon, UK). Five backscattered electron (BE) images were obtained from the file surface under high vacuum chamber conditions, using a 15-kV accelerating voltage and 12-mm working distance, and the area ratio of regions with mean atomic number contrast was determined using digital image processing. The differences among mean values were determined with one-way analysis of variance using file size as independent variable ($a = 0.05$). The elemental compositions of representative locations with mean atomic number contrast were analyzed using EDX spot analysis. Three spectra were collected from the brighter (heavier) locations and three

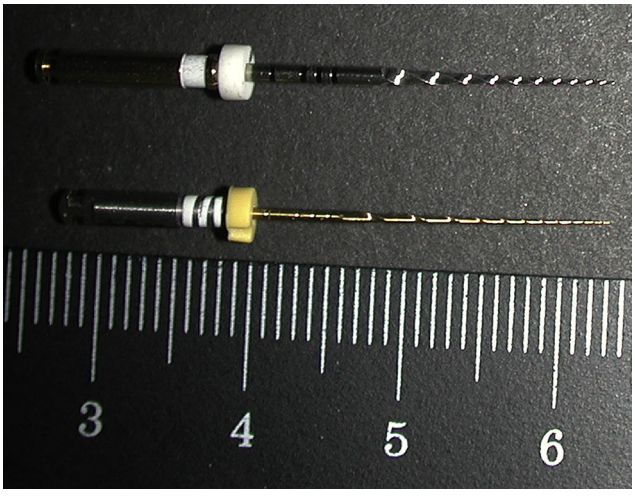

Figure 1 Titanium nitride coated file with the characteristic yellowish color and an uncoated conventional Ni—Ti file. Scale in mm.

from the gray (lighter) locations of each, file and the results were averaged.

The rest of the files (#20, #30, and #40) were embedded in epoxy resin in such a way that their long axis was parallel to the floor (Caldofix; Struers, Ballerup, Denmark). Then their longitudinal sections were prepared and polished using an Argon Ion Beam preparation method (Cross Section Polisher SM 09010; Jeol Ltd.) operating under a 6-kV accelerating voltage and 500-μm ion beam diameter. The cross sections were carbon coated and imaged using BE. The coating thickness was measured in five randomly selected areas starting from the bottom toward the tip of endodontic file. The results were statistically analyzed with one-way analysis of variance using file size as the discriminating variable at the 95% level of significance ($a = 0.05$). EDX spectra were collected operating in spot mode, whereas the elemental distributions at the bulk—coating interface were identified using area and line scan modes. The acquired data were analyzed using the dedicated software (AZtec ver 2.1a; Oxford Instruments). Spot analysis was performed on the coating and bulk area of the endodontic files acquiring five spectra from each location, and the quantitative results were averaged. The elemental distributions of Ni, Ti, N, and O were determined by EDX analysis operating in area scan mode, and the profiles of aforementioned elements were determined from the bulk outward to the surface of the files across a 4.3-μm line using 970 analysis points per micron, a 1540-second acquisition time, and 350 microseconds per point dwell time. The line scan results were smoothed using the AZtec ver 2.1a (Oxford Instruments) software. In both area and line scans, C was not included in the analysis because of its presence in the conductive coating.

Results

Figure 2A illustrates a representative BE image from the cutting surface of the endodontic files showing almost parallel oblong regions with higher mean atomic number contrast, whereas Figure 1B illustrates the aforementioned region differentiated from the rest of the surface after image processing for quantification procedures. No significant differences were identified among the files tested as presented in Table 1. The EDX analysis ($n = 3$) showed that the H regions have relatively decreased Ti and N content compared to the rest of the surface. This is a common finding for the three files tested, as can be seen in the results of Table 1.

Figure 3A presents a representative BE image of the cross section where the coating is distinguished from the bulk, based on the mean atomic number contrast. The cross-sectional analysis illustrated that the coating is characterized by a thin film with a mean thickness of

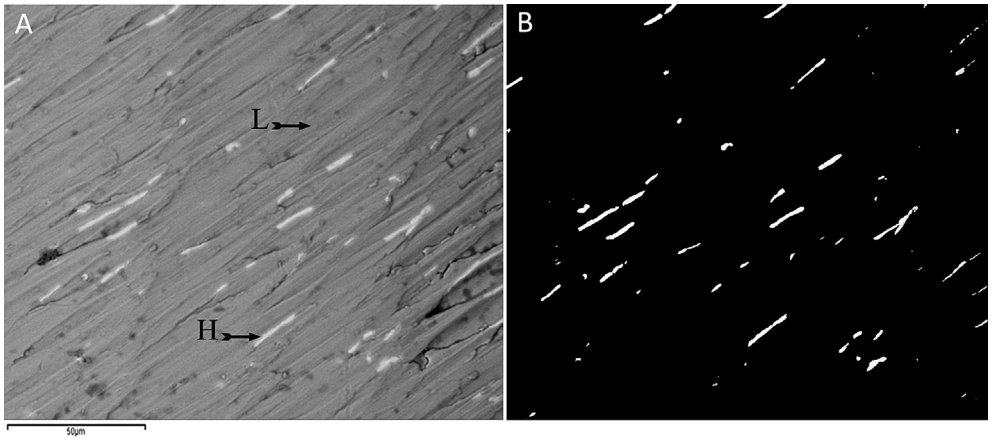

Figure 2 (A) Representative BE image for the surface of as-received files. Parallel oblong regions denote areas with higher mean atomic number (H) compared to the rest of the surface (L). Arrows show representative points of the spot EDX analysis (bar = 50 μm). (B) The oblong regions have been distinguished based on image contrast in BE and marked with white color for further image processing. BE = backscattered electron; EDX = energy-dispersive X-ray spectroscopy.

Table 1 Mean values of elemental composition of low (L) and high (H) (oblong regions) mean atomic number areas on cutting surface of files tested along with the area ratio of H region[a] on file surface and coating thickness.[a]

File no.	L			H			Area ratio of H regions (%)	Coating thickness (μm)
	Ti	Ni	N	Ti	Ni	N		
15	57.6	29.6	13.5	50.6	45.1	5.0	6.5 ± 2.7	
25	57.8	29.0	12.7	50.8	44.8	5.3	7.4 ± 1.9	
35	57.9	28.6	12.6	50.9	44.9	4.9	5.9 ± 2.3	
20								0.33 ± 0.03
30								0.30 ± 0.03
40								0.29 ± 0.02

[a] No differences were identified among different file sizes ($P > 0.05$).

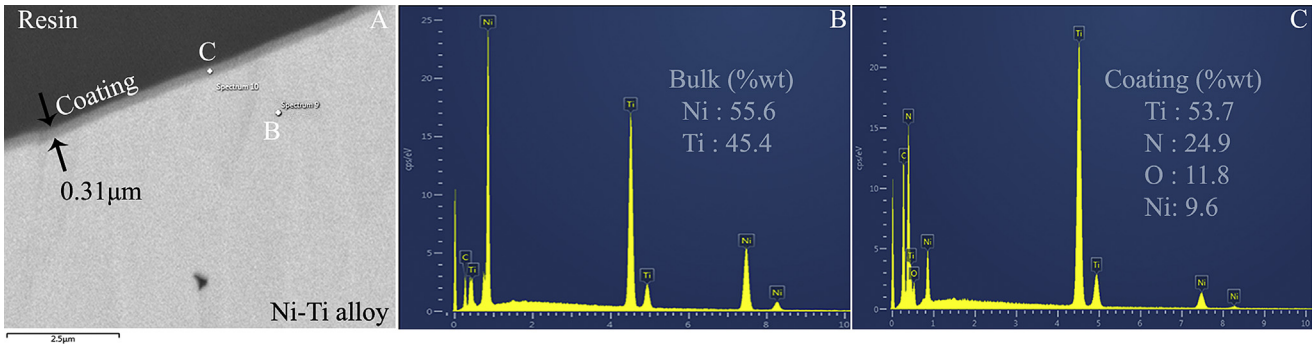

Figure 3 (A) BE image from the cross section where the coating is distinguished from the file and embedding resin. The white points indicate representative points of EDX spot analysis at (C) the coating and (B) the bulk. (Bar = 2.5 μm.) (B) EDX spectrum from the bulk of the file where only Ni and Ti were identified. (C) EDX spectrum taken at C (coating), where N and O were also identified along with Ni and Ti. BE = backscattered electron; EDX = energy-dispersive X-ray spectroscopy.

~0.31 μm without statistical significant differences among the files tested (Table 1). Only Ni and Ti were identified from the spot analysis in the bulk of the Ni—Ti file (Figure 3B), whereas N and O were also found at the coating region (Figure 3C). The quantitative results at the coating show a greater Ti/Ni wt.% ratio (5.5) compared to the bulk (0.8) with a substantial amount of N and O (Figure 3B and C).

The results of area mapping are presented in Figure 4. Ti and Ni illustrate a homogeneous distribution in alloy, and the same is true for O in resin, whereas N shows a constant increase content at the coating region (Figure 4D). Figure 5 depicts the results of line scan analysis for Ti, Ni, N, and O. Ti shows its content peak at the coating/bulk interface and then declines toward the file surface. By contrast, the Ni content begins decreasing about 0.2 μm below the coating/bulk interface, whereas N and O start increasing 0.6 μm and 0.4 μm, respectively, inner to the coating/bulk interface showing their peak content within the coating region.

Discussion

Surface analysis of as-received files revealed a random distribution of oblong regions with a higher mean atomic number (Figure 2), which is appended to the increase in Ni content and decrease in Ti and N content, respectively. Given that Ti and N are components of the coating, these findings might be attributed to decreased coating thickness or to the uneven distribution of coating element themselves. Interestingly, these regions follow the machining marks (Figure 2) of file production, and thus this might be related to the efficacy of the coating production method to provide a uniform coating thickness on a rough surface. Although it is referred that these files have been coated via PVD,[5] it should be noted that PVD is a general term describing a variety of different coating techniques such as arc ion plating, cathodic arc, and radiofrequency sputtering.[1] Furthermore, as the coating method is not reported in

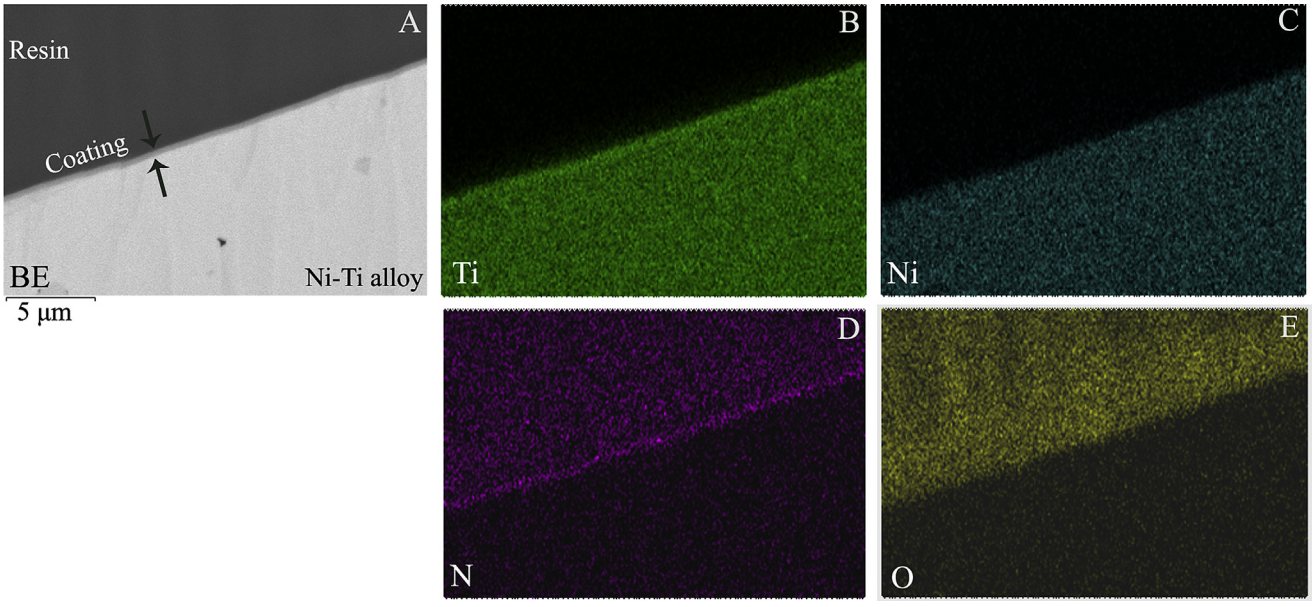

Figure 4 (A) BE image from the cross section analysis of files tested, and corresponding EDX elemental maps for (B) Ti, (C) Ni, (D) N, and (E) O. BE = backscattered electron; EDX = energy-dispersive X-ray spectroscopy.

the manufacturer's literature, the exact nature of the coating application probably remains proprietary.

In order to preserve the quality of the coating and avoid artifacts such as interface detachment, void damage, and uneven surfaces due to different abrasion rates of the different phases with conventional grinding,[15] the Cross Polisher with a penning type ion gun was used in this study to prepare the cross section surfaces. Cross section images showed a well-formed and defined interface between the substrate bulk file and the coating (Figure 3). No differences were found in coating thickness among the files tested (Table 1), implying that the thickness is independent of file size, and thus the coating procedure provides a constant coating thickness for all instrument tested. The mean thickness of the coating was found lower than the range reported (1—7 μm) for PVD technique, a finding that might be appended to technique developments or modifications through the past years.[8]

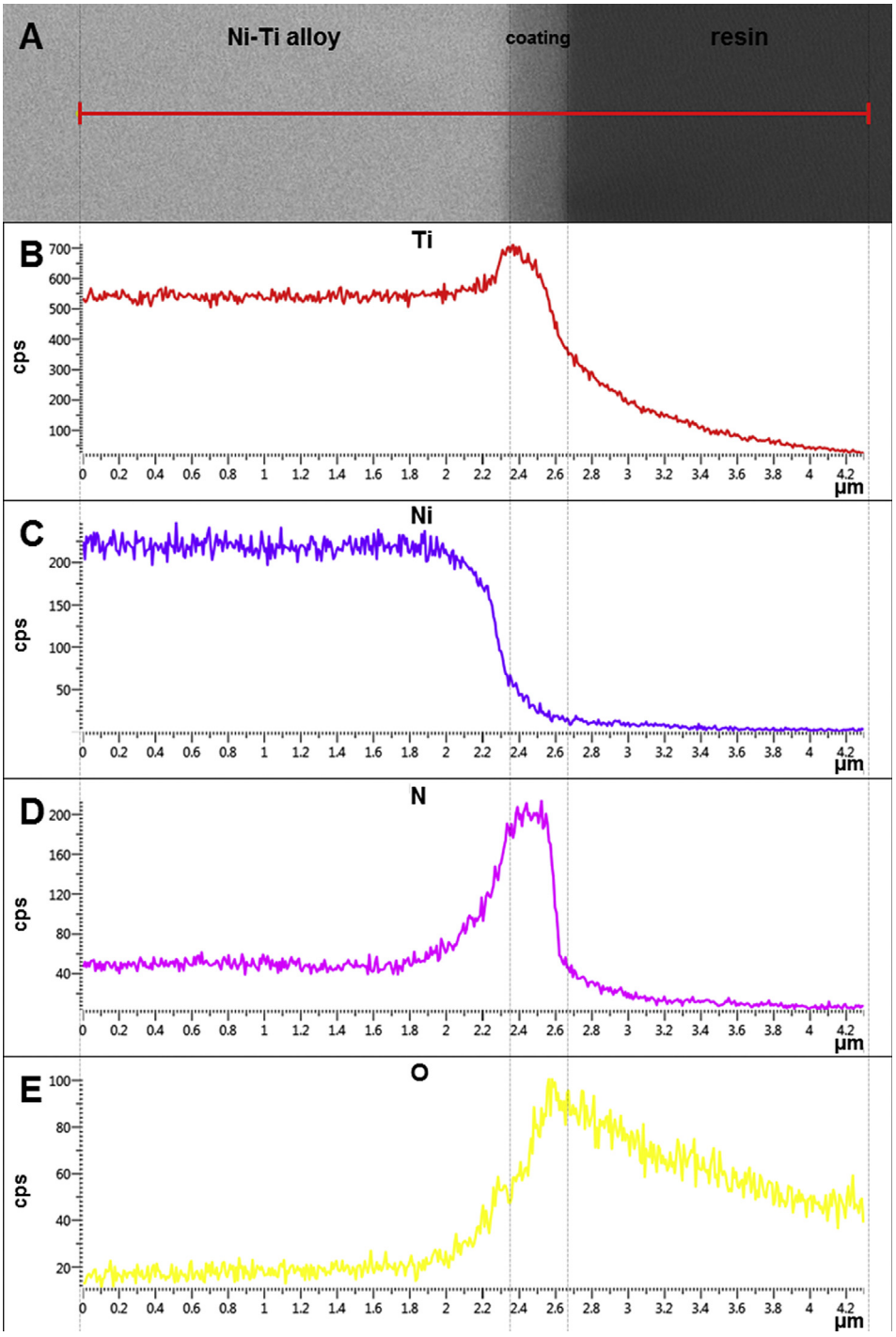

Figure 5 (A) BE image with the line where the line analysis has been carried out, and EDX line profile analyses of (B) Ti, (C) Ni, (D) N, and (E) O. BE = backscattered electron; EDX = energy-dispersive X-ray spectroscopy.

EDX analysis showed that the coating was composed of Ti, Ni, N, and O, whereas only Ni and Ti were identified at the core of the file. Although the qualitative results are presented for both surface and cross-sectional analyses (Figure 3B and C), EDX analysis is mostly used for the qualitative analysis of light elements (such as N) because of their low photo energy, and thus quantitative results in a nonstandard analysis cannot be taken as accurate.[16] However, the X-ray counts of light elements are directly comparable between different locations in surface and cross section analyses as the spectra have been collected under the same conditions (accelerating voltage, beam current, acquisition time, etc.) and have been subjected to the same matrix effect.[16] The presence of N is readily attributed to the TiN coating, whereas the inclusion of O has led others to speculate that oxynitrides may develop in TiN coatings.[17,18] In another study[14] where commercially Ni—Ti files were subjected to various nitriding procedures, X-ray photoelectron spectra analysis illustrated that the surface is dominated by TiN (which gives the surface this characteristic light golden color) along with TiO_2 and traces of NiO. However, the surface composition is strongly dependent on the manufacturing process, and thus the definite identification of specific commercial products needs extensive research with advanced experimental techniques (i.e., X-ray photoelectron spectra, transmission electron microscopy).

X-ray mapping verified the continuous presence of N (Figure 4D) at the coating region, whereas line scan analysis provided interesting data for the variation of elements tested within the coating and possible diffusion into the Ni—Ti alloy. Interestingly, all probed elements showed different profiles with Ti and O exhibiting their peak values at the bulk—coating interface and the external surface, respectively, implying that the formation of different chemical compounds might have taken place. N and O contents begin increasing inner to the coating/bulk interface (Figure 4D and E), denoting the possibility of diffusion of both elements within the bulk of the Ni—Ti file, most likely triggered by the coating procedure. Further research is required to reveal the chemical state of the aforementioned elements at the coating and subcoating region.

Although experimental and prototype coated files have been found to be improved over conventional files in terms of cutting or cleaning ability, wear, corrosion resistance, fatigue life, and shaping ability further verification in commercialized varieties is required. The study of the sustainability of the coating after *in vivo* use through full successive clinical chemomechanical treatments should be added to the previous comments, as the hard coating might crack and debond from the flexible core of Ni—Ti file, an approach that has not yet been implemented in previous reports. Nonetheless, the concept of a hard surface coated but also flexible Ni—Ti endodontic files is very promising, and the applications of an effective coating may open a new era in endodontic file production.

Conflicts of interest

The authors have no conflicts of interest relevant to this article.

Acknowledgments

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