Review Article

Revolutionizing endodontics: Advancements in nickel–titanium instrument surfaces

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Abstract

Nickel–titanium (NiTi) instruments have become the backbone of endodontics due to their exceptional properties, superelasticity, and shape memory. However, challenges such as unexpected breakage, poor cutting efficiency, and corrosion have prompted researchers to explore innovative surface modifications to enhance their performance. This comprehensive review discusses the latest advancements in NiTi metallurgy and their impact on rotary NiTi file systems. Various surface treatment techniques, including ion implantation, cryogenic treatment (CT), thermal nitridation, electropolishing, and physical or chemical vapor deposition, have been investigated to minimize defects, boost surface hardness, and improve cyclic fatigue resistance. Ion implantation has shown promise by increasing wear resistance and cutting efficiency through nitrogen ion incorporation. Thermal nitridation has successfully formed titanium nitride (TiN) coatings, resulting in improved corrosion resistance and cutting efficiency. CT has demonstrated increased cutting efficiency and overall strength by creating a martensite transformation and finer carbide particles. Electropolishing has yielded mixed results, providing smoother surfaces but varying impacts on fatigue resistance. Physical or chemical vapor deposition has proven effective in forming TiN coatings, enhancing hardness and wear resistance. Furthermore, the concept of surface functionalization with silver ions for antibacterial properties has been explored. These advancements present an exciting future for endodontic procedures, offering the potential for enhanced NiTi instruments with improved performance, durability, and patient outcomes.

Keywords: Cryogenic treatments; ion implantation; nickel–titanium alloy; surface modifications; surface treatments; thermal treatment

INTRODUCTION

Nickel–titanium (NiTi) alloy has extensively been utilized as the primary material for producing endodontic instruments. Over time, the demand for NiTi instruments did not drop but, rather, experienced a resurgence. This rebound interest stems from applying contemporary research methods and tools from diverse fields, turning it into an interdisciplinary field of study. In 1988, Walia *et al*. first introduced NiTi files to the field of endodontics.[1] Initially, Civjan *et al*.[2] proposed the application of NiTi alloy for crafting rotary and hand files. NiTi rotary files gained popularity due to their ability to shape and debride the canals with greater precision and lesser procedural errors than stainless steel (SS) hand instruments.[3] Although, these files are susceptible to unexpected breakage. Flexural and torsional fractures are two separate fracture modes for NiTi files. Flexural fractures develop due to the files in curved canals experiencing cyclic fatigue. When NiTi files are loaded and unloaded repeatedly during instrumentation, a recurrent phase transition occurs that finally causes torsional fracture once the instrument has passed the point of irreversible plastic deformation.[4]

To enhance their performance, there is a demand for new materials and manufacturing techniques for NiTi

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rotary instruments. The development of novel rotary endodontic instruments with superior mechanical qualities has been popular in recent years due to the realization that the microstructural changes brought about by thermomechanical treatments can regulate the phase transformations happening in equiatomic NiTi alloys. NiTi instruments have intrinsic flaws that occur during the manufacturing process;[5] hence, efforts have been made to improve their surface properties. Different surface changes have been used to lower or eliminate flaws, boost surface hardness or flexibility, enhance cycle fatigue resistance, and improve cutting effectiveness. Various techniques discussed in this review have been used to give NiTi alloys beneficial properties for the best performance as an endodontic file.

To address material-related concerns with NiTi alloy and the manufacturing of instruments, such as poor cutting efficiency and failure due to fatigue caused by defects, surface changes have been investigated and modified. This review focuses on the latest advancements in NiTi metallurgy and its effect on rotary NiTi files, aiming to pave the way for even more effective and reliable endodontic procedures.

SURFACE CHARACTERISTICS OF NICKEL–TITANIUM ALLOY

The surface of NiTi instruments primarily comprises titanium oxides (TiO_2), carbon, and oxygen, with less quantities of nickel oxides (NiO and Ni_2O_3) and metallic nickel (Ni).[6] The thickness of the oxide layer can vary between 2 and 20 nm, and the surface chemistry and the amount of Ni may differ widely depending on the preparation method.[7] Ni disintegrates more readily as compared to titanium (Ti) due to the less stable nature of its oxide. The superficial layers of NiTi wires exhibit uneven features represented as long island-like formations, suggesting selective dissolution of Ni.[8]

Shabalovskaya[9] observed that the Ti:Ni ratio on the wire surface was 5.5 after mechanical polishing, indicating the presence of five more times Ti on the surface than Ni. However, after boiling or autoclaving the wire in water, the Ti: Ni ratio scaled to 23.4–33.1, and the Ni content was reduced. Similar results were obtained by Hanawa *et al*.,[6] who found that after immersion in neutral electrolyte solution for 30 days, the Ti: Ni ratio in the polished samples rose from 5.8 to 91. Although the titanium–aluminum–vanadium alloy (Ti_6Al_4V) in their investigation only had 6% aluminum compared to 50% Ni in NiTi, the surface of the alloy had aluminum levels similar to those in NiTi. However, some chromium and iron were discovered on the exterior of SS, which was devoid of Ni.

Due to the presence of a persistent TiO_2 layer, pure Ti and specific Ti alloys are regarded as extremely biocompatible materials.[7] The oxide layer that forms on a Ti implant during implantation expands and takes up minerals and other substances from tissue fluids, resulting in surface remodeling. Hanawa *et al*.[6] discovered that the calcium phosphate and Ti dioxide layers make up the oxide layer on implants. On an inert oxide layer, calcium phosphate is specifically produced. This layer had a Ca:P ratio that was similar to hydroxyapatite and was denser on pure Ti than Ti alloys (including NiTi). However, the calcium phosphates generated on NiTi or Ti_6Al_4V were less akin to hydroxyapatite. This is probably because Ni is present on the exterior of NiTi alloy, and aluminum is present on the surface of Ti_6Al_4V, which may have impacted these results. Similar calcium phosphate layers also exist in SS, although they form more slowly and differently than they do in NiTi.[6,10,11]

SURFACE MODIFICATIONS OF NICKEL–TITANIUM ALLOYS

Numerous strategies have been employed to improve the surface properties of NiTi instruments, aiming to reduce their inherent flaws, enhance surface hardness and flexibility, and improve resistance to cyclic fatigue and cutting efficiency in endodontic procedures.[12] As summarized in Table 1, some of them are:

A. Ion implantation
    a) Implantation of nitrogen (N_2), argon (Ar), and boron (B) ions
    b) Plasma immersion ion implantation (PIII).

B. Thermal nitridation
    a) Surface coating with titanium nitride (TiN) layer
    b) Powder immersion reaction-assisted coating (PIRAC).

C. Cryogenic therapy
D. Electropolishing
E. Vapor deposition
    a) Physical vapor deposition (PVD)
        i. Arc evaporation
        ii. Magnetron sputtering
        iii. Ion plating.
    b) Chemical vapor deposition.

F. Surface functionalization
    a) Silver ion coating.

Ion implantation

Several efforts have been made to minimize the liberation of Ni from NiTi while preserving the mechanical features of the bulk material. Ion implantation is one such coating

Table 1: Studies included in the review and their results obtained

Surface modification	Author	Year	Method	Result
Ion implantation	Gavini *et al.*[13]	2010	Nitrogen ion implantation	Increases the number of CTF
	Wolle *et al.*[14]	2009	Argon and nitrogen ion implantation	Argon ion implanted file showed double the number of CTF than nitrogen ion implanted file
	Rapisarda *et al.*[15]	2001	Nitrogen ion implantation	Increased wear resistance
	Conrad *et al.*[16]	1987	PIII of TiN	Increased wear resistance
	Tendys *et al.*[17]	1988		
Thermal nitridation	Rapisarda *et al.*[18]	2000	TiN coating	Improved cutting ability
	Lin *et al.*[19]	2007	TiN coating	Greater corrosion resistance when exposed to 5.25% NaOCl
	Li *et al.*[20]	2006	TiN coating	Increased cutting efficiency and corrosion resistance
Cryogenic therapy	Kim *et al.*[21]	2005	Cryogenic therapy	Higher microhardness, increased austenitic phase, increased cutting efficiency
	Vinoth Kumar *et al.*[22]	2007	Deep CT	Improved cutting efficiency, no effect on wear resistance
	George *et al.*[23]	2011	Deep CT	Increased cyclic fatigue resistance
Electropolishing	Anderson *et al.*[24]	2007	Electropolishing	Increased cyclic fatigue resistance
	Tripi *et al.*[25]	2006		
	da Silva *et al.*[26]	2013		
	Lopes *et al.*[27]	2010		
	Condorelli *et al.*[28]			
	Praisarnti *et al.*[29]			
	Herold *et al.*[30]	2007	Electropolishing	Does not prevent microfractures
	Bui *et al.*[31]	2008	Electropolishing	Electropolished files less resistant to cyclic fatigue
	Kaul *et al.*[32]	2014	Electropolishing	Eliminated manufacturing flaws but produced a weak surface highly vulnerable to fresh crack development
Vapor deposition	Schäfer[33]	2002	PVD to NiTi K-files	26.2% increase in cutting efficiency
	Chi *et al.*[34]	2017	Titanium–zirconium-boron surface layer via PVD	Highly smooth file geometry with greater cyclic fatigue resistance
	Bonaccorso *et al.*[35]	2008	PVD and immersion in sodium chloride	Enhanced corrosion resistance, and better pitting resistance
	Qaed *et al.*[36]	2018	PVD	Electropolished files performed better than physical vapor-deposited files
Surface functionalization	Cora *et al.*[37]	2020	2% silver ion dip-coating	Increased efficiency against *Enterococcus faecalis* without influencing cutting efficiency

CT: Cryogenic treatment, TiN: Titanium nitride, PIII: Plasma immersion ion implantation, CTF: Cycles to fracture, PVD: Physical vapor deposition, NiTi: Nickel–titanium

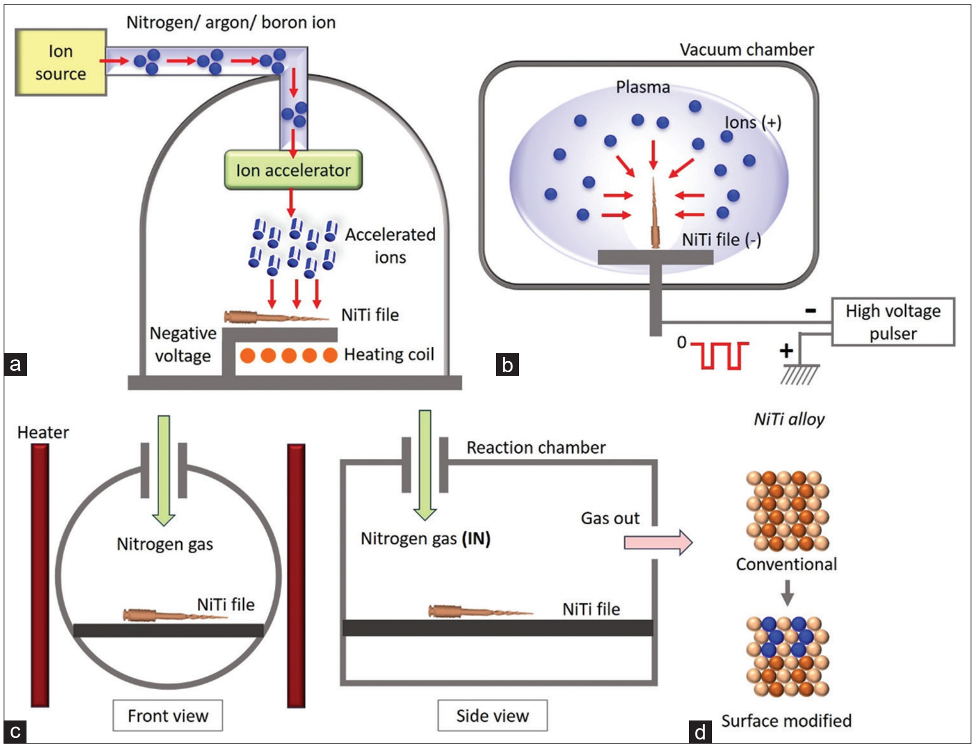

Figure 1: Illustration of various surface treatments. (a) Ion implantation, (b) plasma immersion ion implantation, (c) thermal nitridation, (d) surface morphology of NiTi file before and after surface treatment. NiTi: Nickel–titanium

technique. As shown in Figure 1a, this involves bombarding gaseous atoms that have been voltage-accelerated into ions such that they get buried beneath the surface of the substrate. The accelerating voltage affects the depth to which they are buried. The end result produces a series of dislocations that increase the material's durability.[14] Various ions that can be implanted on endodontic files are N_2, Ar, and B.

With the implantation of N_2 ion, the hardness of endodontic files is decreased, while resistance to wear, cutting efficiency, and cyclic fatigue resistance is increased.[13,15,18,38] Gavini *et al*.[13] demonstrated that compared to nonimplanted (381 cycles) and annealed files (428 cycles), N_2 ion-implanted instruments had a considerably greater number of cycles to fracture (CTF) (510 cycles). Wolle *et al*.[14] examined the impact produced on file morphology by Ar and N_2 ion implantation. The studies demonstrated the potential growth and spread of cracks and their resistance to cycle fatigue. While endodontic files ingrained with N_2 performed inferiorly in the fatigue test, merely attaining approximately half the mean CTF, authors found files ingrained with Ar have higher CTF than endodontic files without any alterations. Contrary to findings from Rapisarda *et al*.,[15] who showed a rise in files' wear resistance ingrained with N_2 ions, this investigation did not discover any significant development or propagation of cracks.

This might result from N_2's higher atomic mass, which restricts the generation of point defects within the crystalline structure. Additionally, N_2 forms an exceptionally hard material called TiN when combined with Ti in the file, preventing microfractures.[15] Clinically, a surge in wear resistance may extend the instrument's life while retaining its accuracy and blade shape after usage and lowering the danger of instrument fracture.

To successfully increase the surface hardness of NiTi alloys, Lee *et al*. inserted B ions into them using a nonequilibrium technique.[39] N_2 was substituted with B because Ti-B has greater mechanical strength than Ti-N. The therapeutic applicability of the findings is constrained using a flatter polycrystalline substrate of NiTi alloy in this investigation rather than an endodontic file.

In the late 1980s, Conrad *et al*.[16] and Tendys *et al*.[17] first developed PIII. In this procedure, as shown in Figure 1b, the specimen is placed in a chamber surrounded by plasma ions. A powerful negative pulsating voltage is then used to suck the ions from the plasma, accelerate them, and batter them onto the object's surface. This method only alters surface features by adding a coating of TiN, which gives items a golden appearance. As a result, wear resistance is increased without sacrificing the material's natural flexibility or microstructure.[40,41]

Thermal nitridation

Thermal nitridation is another method for producing a hard surface layer that increases wear resistance and surface hardness, as shown in Figure 1c. The sample is heated up thermally in an N_2 atmosphere, typically between 200 and 500°C,[18,19] which coats the NiTi files with a layer of TiN, as shown in Figure 1d. Ion implantation and thermal nitridation, two alternative TiN surface treatments, were contrasted by Rapisarda *et al*.[18] Compared to unaltered files, both procedures demonstrated a higher TiN presence, while ion implantation demonstrated a higher N_2-to-Ti ratio. Ion implantation showcased a higher cutting efficiency than thermal nitridation, but both techniques had improved cutting ability compared to no surface treatment.[18]

Shenhar *et al*.[42] and Huang *et al*.[43] demonstrated that the presence of a TiN coating significantly enhanced the resistance to corrosion of Ti and Ti alloys when exposed to a corrosive environment. When exposed to 5.25% sodium hypochlorite, Lin *et al*.[19] showed that including TiN on NiTi endodontic files considerably boosted corrosion resistance. The highest corrosion resistance was achieved at 300°C nitriding temperatures, although following treatment, NiTi's superelastic characteristics were lost. As a result, nitriding at a temperature of 250°C was advised for usage in clinical settings.[19] Li *et al*.'s[20] investigation of thermal nitridation at various temperatures revealed that the presence of TiN increased cutting effectiveness and corrosion resistance.

PIRAC is another technique for creating a layer of TiN. Substrates are annealed in enclosed steel foil vessels at less pressure and high temperatures (800°C–1100°C).[44,45] An N_2-rich layer with a thin outer layer of TiN and a thicker layer of Ti_2Ni is formed on the surface of the sample due to the diffusion of highly reactive monatomic N2.[46] It is noticeable that PIRAC layers have good adherence to the substrate and are comparable to oxide layers on NiTi alloys. Although this method has been applied to biomedical NiTi alloys, it has not been explicitly researched on NiTi endodontic files.

Cryogenic therapy of nickel-titanium alloys

As shown in Figure 2a, cryogenic treatment (CT) is a manufacturing process recommended to enhance the surface hardness and thermal stability of metals.[47] The optimal temperature range for this therapy is typically between − 60°C and − 80°C, which may vary according to the material and specific quenching parameters present.[47] Over the past three decades, reports have shown significant advantages of exposing metals used for industrial purposes to CT.[47-49]

CT is a relatively newer cooling approach involving immersing the metal in a super-cooled bath of liquid N_2 at extremely low temperatures of around − 196°C (−320°F).[47,48]

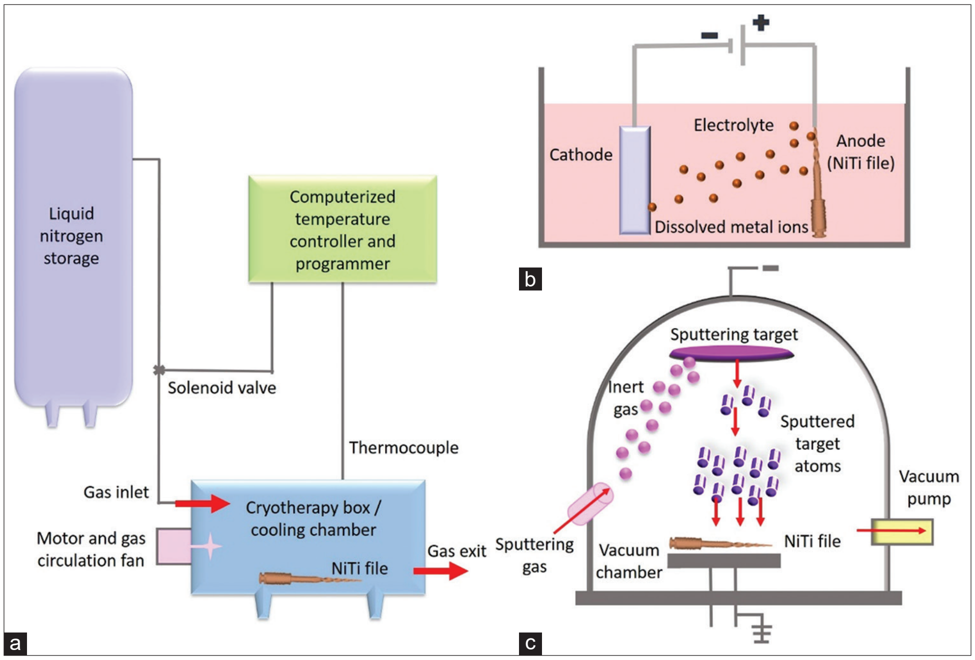

Figure 2: Illustration of various surface modifications. (a) Cryogenic therapy, (b) electropolishing, (c) physical vapor deposition. NiTi: Nickel–titanium

The metal is then allowed to gradually warm to room temperature.[49,50] Compared to traditional cold treatment, CT offers more favorable effects.[51] The advantages include increased cutting efficiency and strength of the alloy.[47,49] Additionally, CT is a cost-effective therapy that influences the whole cross-section of the alloy, unlike surface treatments such as vapor deposition and ion implantation, which only impact the surface.[48]

During CT, two mechanisms can change the metal properties. The first mechanism follows CT and entails a more thorough martensite transition from the austenite phase.[50] The next mechanism is the precipitation of smaller carbide particles inside the crystalline structure.[49] However, there is some debate about which mechanism plays the primary role in these changes.

Regarding NiTi rotary instruments, there have been relatively few studies on CT. Kim *et al*.[21] assessed the impact of cryogenic therapy on the cutting efficiency, composition, and microhardness of NiTi files. Their results revealed that cryogenically modified files exhibited considerably higher microhardness than controls. The composition of the test and control groups was 56% Ni (by weight), 44% Ti (by weight), and no N, with the bulk of the material in the austenite phase. The deep dry CT greatly improved the cutting effectiveness of NiTi instruments but had no appreciable impact on wear resistance, according to a different study by Vinothkumar *et al*.[22] A deep CT considerably increased the cyclic fatigue resistance of NiTi rotary files, according to George *et al*.'s[23] research.

Electropolishing

As shown in Figure 2b, electropolishing is an electrochemical process that removes surface imperfections.[52] A direct current is passed through the solution while the file (anode) is submerged in an electrolytic bath with a cathode that is kept at a specific temperature.[53] As a protective layer, a surface oxide layer is created, which improves corrosion resistance and cyclic fatigue resistance, and there is a reduction in surface residual stress.[5,12,24,54,55] It is debatable if electropolishing actually increases the resistance to corrosion and fatigue life of NiTi instruments. There is general agreement that electropolishing improves the endodontic file's surface texture, making it smoother.[25,30,32,35,56,57]

Compared to nonelectropolished files, electropolished instruments need a larger potential to form pitting, indicating greater corrosion resistance.[35] While the existence of a corrosion pit was linked to the onset of cracks, other studies revealed that electropolishing did not increase corrosion resistance.[56,57] Various studies by Anderson *et al*.,[24] Tripi *et al*.,[25] da Silva *et al*.,[26] Lopes *et al*.,[27] Condorelli *et al*.,[28] and Praisarnti *et al*.[29] have shown that electropolishing increases cycle fatigue resistance. Larger groove flaws lead to fewer cycles till fracture,[58] whereas surface irregularities would act as places of stress concentration and lead to crack initiation.[24] In contrast, Herold *et al*.[30] discovered that when compared to regular, untreated ProFiles, electropolishing (EndoSequence) does not prevent microfractures. Bui *et al*.[31] discovered, on the other hand, that in simulated canals made of plastic blocks, electropolished profiles were considerably less resistant to cycle fatigue than conventional ProFiles. When utilizing electropolished files, greater maximum torque values were needed,[59] suggesting that electropolishing may level and dull the cutting edges, necessitating a larger torque to obtain the same amount of preparation. Examination revealed that the crack lines were occasionally inconsistent with the machined grooves.[60]

While electropolishing eliminated all manufacturing flaws, Kaul *et al*.[32] discovered a weak surface and highly vulnerable to developing fresh cracks. Altogether, many other investigations indicated that electropolished instruments had not shown higher resilience to cyclic fatigue than any other instrument.[61] Electropolishing had a minimal impact on cutting effectiveness and torsional resistance.[24,26,31] In conclusion, electropolishing gives endodontic files a smoother finish; however, the evidence for the advantages of this surface treatment is inconsistent.

Physical or chemical vapor deposition

Since the late 1980s, medical devices have been coated using the PVD technique to increase wear resistance.[62] PVD has three main types: arc evaporation, magnetron sputtering, and ion plating.[33] PVD produces a dense, homogeneous layer that is highly resistant to corrosion, has enhanced surface hardness, and is biocompatible.[33] The cathodic arc evaporation process is frequently utilized for the best coating to metal adherence. As a result, TiN forms a hard coating over the surface, as shown in Figure 2c.

Using this method, a thin layer of fine-grained TiN film is formed at low temperatures over the surface of files. This TiN layer can increase wear resistance, surface hardness, and cutting efficiency.[15,18] The surface hardness can reach 2200 VHD when the coating thickness ranges between 1 and 7 microns. Surface imperfections, fissures, and potential residual stresses are eliminated by forming a continuous amorphous coating over the file's surface, extending the life of the endodontic instrument.[63] When Schafer initially applied PVD to NiTi K-files, he discovered a 26.2% rise in cutting efficiency compared to files without coating.[33] Chi *et al*. added a unique Ti-zirconium-B (TiZB) surface layer via PVD, resulting in a TiZB film with a highly smooth file geometry and greater cyclic fatigue resistance than untreated files.[34] In PVD instruments, Bonaccorso *et al*.[35] showed enhanced corrosion resistance. The study discovered that when PVD files were submerged in sodium chloride solution for 1.5 h, they had better pitting resistance than electropolished or nonelectropolished files. Since sodium chloride solutions are not usually employed in endodontic treatments, the findings of this study cannot be easily applied to clinical settings. However, electropolished files outperformed PVD files, according to Qaed *et al*.[36]

At high temperatures of 300°C, chemical vapor deposition (CVD) also forms a superficial layer made up of TiN.[64,65] Early research proved metal-organic CVD as the elected technique as it can enhance the Ni: Ti ratio on the substrate's surface by up to twofold.[65] While both CVD and PVD may provide a tough surface layer to NiTi devices, PVD deposits films with clearly defined grains, whereas CVD produces uninterrupted coatings of amorphous materials having weak crystalline structures.[64] Notably, the superficial layers may become exposed as the file's cutting edges deteriorate,[33] and the fragments may end up trapped within the canal space. Toxic effects may arise from the liberation of these nanoparticles or metal ions.[66]

Surface functionalization of nickel-titanium endodontic files

The objective of surface functionalization is to either block a potentially harmful reaction or to elicit a desired response. To reinforce the NiTi wire, several coatings have been used.[67] Early Teflon and polyethylene coatings have been shown to increase corrosion resistance.[68] Rhodium coatings with low reflectivity and epoxy resin have been used as surface coatings. Compared to uncoated NiTi wires, these coatings can minimize surface roughness.[69] Damage to the surface morphology, however, could be harmful in an endodontic situation because it could cause fractured particles from the surface coating to get dislodged inside the root canal space or move into the periapical area, potentially causing a foreign body response.[70] Most endodontic studies on surface modifications have mainly concentrated on the geometry and shape created by these files, such as conicity, taper, and centering ability, as well as their mechanical features, such as metallurgy, flexibility, cyclic fatigue, torsional fatigue, cutting efficiencies, and so on.

A single study has probed into the idea of giving endodontic instruments a new use beyond their current capacity of shaping the root canal and clearing away the debris. Cora *et al*.[37] coated the surface of NiTi rotary files with silver ions and examined their antibacterial properties. They used the dip-coating process at 25 or 50 mm/min for coating the ProTaper Universal NiTi files with a silane-based, silver-complex solution (2% silver ion coating).[37] *Enterococcus faecalis* was used as a test subject for its antibacterial activity. Cultures were taken from the sample and incubated; then, the bacterial colony count was recorded. The debris lost in clear resin blocks after creating an artificial root canal was used to compare the cutting effectiveness of coated and uncoated files.[37] Additionally, they examined the files using scanning electron microscopy and observed that the silver ion surface coating did not influence the cutting efficacy of rotary NiTi endodontic file, while it was effective against *E. faecalis*. This encapsulates the conceptual framework and potential for functionalizing NiTi rotary files in the future.

CONCLUSION

NiTi instruments have seen a resurgence in endodontics, driven by cutting-edge research and interdisciplinary approaches. Exciting surface modifications, such as N_2 ion implantation for wear and fatigue resistance and PIII for a durable TiN layer, are elevating performance. Thermal nitridation creates a corrosion-resistant TiN coating, while CT at super-cooled temps enhances strength. Electropolishing offers smoother surfaces, but the impact on fatigue varies. Physical or chemical vapor deposition provides tough TiN coatings. Surface functionalization with silver ions shows potential for antibacterial properties. These innovations promise a bright future for enhanced endodontic procedures.

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Conflicts of interest

There are no conflicts of interest.

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