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Advancing Nitinol: From heat treatment to surface functionalization for nickel–titanium (NiTi) instruments in endodontics

Wai-Sze Chan, Karan Gulati *, Ove A. Peters *

The University of Queensland, School of Dentistry, Herston, QLD, 4006, Australia

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A B S T R A C T

Nickel-titanium (NiTi) alloy has been extensively researched in endodontics, particularly in cleaning and shaping the root canal system. Research advances have primarily focused on the design, shape, and geometry of the NiTi files as well as metallurgy and mechanical properties. So far, extensive investigations have been made surrounding surface and thermomechanical treatments, however, limited work has been done in the realm of surface functionalization to augment its performance in endodontics. This review summarizes the unique characteristics, current use, and latest developments in thermomechanically treated NiTi endodontic files. It discusses recent improvements in nano-engineering and the possibility of customizing the NiTi file surface for added functionalization. Whilst clinical translation of this technology has yet to be fully realized, future research direction will lie in the use of nanotechnology.

1. Introduction

Root canal treatment (RCT) is a routine dental procedure for the management and prevention of apical periodontitis (AP) [1]. AP is characterized by inflammation and ultimately destruction of the pulp and tissues surrounding the apex of the tooth from bacterial toxin infiltration, noxious metabolic by-products or pathogens and microorganisms that invade into the tooth, most commonly from caries [2–5]. It can present with or without apical radiolucency and may have symptoms of pain on biting and/or percussion or palpation [6].

Diagnosis and management of AP is crucial to the overall health and well-being of an individual. A recent meta-analysis found a high global prevalence of AP with pooled samples indicating that 52% of individuals had at least one tooth with AP [7]. Further, a higher prevalence of AP was found in developing countries and individuals with systemic conditions [7].

Treatment of AP typically involves cleaning and shaping the root canal system using instruments such as endodontic files. Endodontic files have been designed to remove infected/contaminated soft- and hard-tissue debris and shape the root dentin [8]. This allows penetration of irrigants (such as sodium hypochlorite (NaOCl) and ethylenediaminetetraacetic acid (EDTA)) to further disinfect the canal space, allowing delivery of medicated dressings such as calcium hydroxide [9] and subsequent sealing of the canal space through obturation [1].

Development and design of endodontic files have undergone substantial changes from the first root canal broach file made from watch springs in 1838 [10]. Instruments are now commonly made from stainless steel (SS) or nickel-titanium (NiTi or Nitinol) alloy. SS wire blanks are ground and twisted to create the size, shape, and design [11]. Conversely, NiTi wires are micro-milled and more recently shaped by electric discharge machining (EDM) to achieve more complex shapes [12]. SS endodontic files were originally selected for their high resistance to fracture and high cutting efficiency [13,14]. However, due to the inherent stiffness of the alloy, these files have a tendency towards straightening in curved canals [15,16]. The rigidity of SS files also increases the risk of iatrogenic events such as: deviations/transportations within the canal (e.g. ledging, elbows, zips, strips), and perforations due to the greater filing action on the inner curve wall [17].

More flexible NiTi files were pioneered by Walia et al. in 1988, which were shown to have less risk of canal transportation [18]. Engine driven endodontic instruments were then introduced and demonstrated greater efficiency and speed of use compared to hand instrumentation [19]. Further technological advancement in metallurgy and ongoing design adaptations have allowed manufacturers to improve instruments through surface and mechanical property changes.

Improvements in endodontic files have mainly focused on mechanical properties such as cutting efficiency and resistance to fracture.

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* Corresponding authors.
E-mail addresses: k.gulati@uq.edu.au (K. Gulati), o.peters@uq.edu.au (O.A. Peters).

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Abbreviations

RCT	root canal treatment
AP	apical periodontitis
SS	stainless steel
NiTi	nickel-titanium
EDM	electric discharge machining
Ni	nickel
Ti	titanium
TTR	transformation temperature range
Ms	martensite start
Mf	martensite finish
As	austenite start
Af	austenite finish
R-phase	rhombohedral phase
SEM	scanning electron microscope
VHN	Vickers Hardness Number
NaOCl	sodium hypochlorite
EDTA	ethylenediaminetetraacetic acid
F-file	Finishing File PlasticEndo
TF	Twisted-File
TFA	Twisted-File Adaptive
CM-wire	controlled memory wire
HCM	Hyflex Controlled Memory
HEDM	Hyflex electric discharge machining
TYP	TYPHOON Inifite Flex
DSC	differential scanning calorimetry
Rf	R-phase finish
Rs	R-phase start
CryoT	cryogenic treatment
N or N2	nitrogen
MaxWire	Martensite-Austenite-electropolish-fileX
Ar	argon
PIII	plasma immersion ion implantation
TiN	titanium nitride
PIRAC	powder immersion reaction assisted coating
DC	direct current
PVD	physical vapor deposition
TiC	titanium carbide
TiCN	titanium-carbon-nitride
TiAlN	titanium aluminium nitride
CVD	chemical vapor deposition
NT	nanotubes
NP	nanopores
NS	nanospindles
H2O	water
NH4F	ammonium fluoride
NiO	nickel oxide
F^-	flouride
Cl	chloride
HCl	hydrochloric acid
PLGA	poly(lactic-co-glycolic acid)
USA	United States of America
CA	California
NJ	New Jersey
CT	Connecticut
OK	Oklahoma
TN	Tennessee
NV	Nevada
IL	Illinois

However, there is only sparse research on further functionalizing NiTi endodontic files beyond its mechanical properties. By definition, surface functionalization is the process of adding new functions, features, capabilities or properties to a material by changing the surface chemistry of the material [20].

Diverse applications of NiTi alloys in medicine requiring specific functionality are well documented [21,22]. One example of its use is in permanently implanted NiTi intravascular prostheses (stents), they are able to self-expand after implantation to recover the lumen space in vessels [21]. Surface modifications of these NiTi stents have improved its function by facilitating endothelial cell adhesion, proliferation and migration for faster healing after implantation [21,22]. The purpose of this review is to highlight aspects of current modifications of rotary endodontic files, as well as other applications and modifications of NiTi alloy within and outside of dentistry (Fig. 1). In addition, we will also discuss the potential prospects and possible future developments with reference to endodontic applications.

2. Metallurgy of nickel–titanium alloy

The application of NiTi in dentistry and specifically endodontics has been reviewed before, detailing metallurgical properties of the alloy, its' structure, martensitic transformation ability and its evolutionary design [11,12,23–25]. NiTi alloys used in endodontic instruments contain

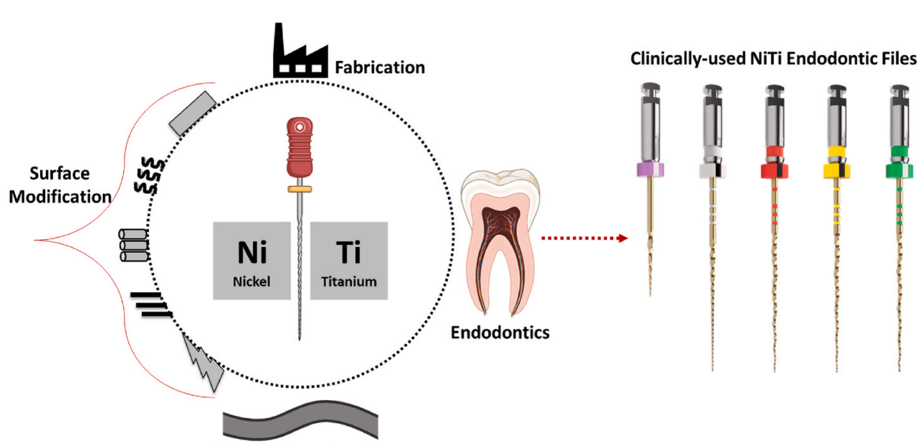

Fig. 1. Article overview. Schematic representation of the NiTi alloy endodontic file (nitinol) including manufacturing, shape memory function and advanced surface modification. Photo of TruNatomy (TN; Dentsply Sirona, Ballaigues, Switzerland) endodontic files (Color image).

Table 1
Comparison of manual SS files and rotary NiTi files.

Material	Advantages	Limitations	Current Trend
Manual SS Composition[a]: • 65.9–72% Iron • 17–20% Chromium • 8–10.5% Nickel • 2% Manganese (max.) • 1% Silicon (max.) • 0–0.6% Molybdenum	• SS has greater hardness compared to NiTi (SS 546~673HV [37] versus NiTi 313~481HV [38,39]). • Greater torsional strength [40]. • Greater cutting efficiency [41]. • Greater fracture resistance [19]. • High resistance to fracture by bending [13]. • Lower cost compared to NiTi endodontic files [1]. • High corrosion resistance in the presence of irrigation solutions [42].	• Greater clockwise rotation at failure for SS files than NiTi files [43]. • More rigid, greater risk of procedural errors [16,44,45]. • Greater transportation and straightening of canal after preparation from original canal shape [45–48]. • Less predictable canal shape after preparation, with greater difficulty in obturating and sealing the canal [8]. • Incomplete debridement of all canal walls [1,44,49].	Limited to use as manual hand instruments. Common uses: locating canal openings, passively scout the first few millimeters into the root canal, maintain patency of the canal and glide path[b].
Rotary NiTi Composition[a]: • 56% Ni • 44% Ti • <2% Cobalt	• Higher torque at failure with larger tapered NiTi files compared to SS. However lower torque at failure with more narrow tapers. • Greater centering ability, limiting risk of transportation [45,47,50]. • Reduced procedural errors [16,45]. • Superelasticity, and increased flexibility, able to be bent without irreversible deformation and retain its original form [18]. • Faster preparation time compared to SS [44, 51–54]. • More predictable canal shape [44,48]. • Less apical extrusion [55]. • Reduced loss of length from ledging or straightening effect [56]. • Greater success rates in inexperienced users compared to manual SS instrumentation [16, 54,57]. • Improved technical quality [57]. • Ideal taper canal form for obturation and seal [28]. • High corrosion resistance in the presence of irrigation solutions [42].	• Additional motor required for use and higher cost compared to SS [1]. • Greater counter-clockwise rotation at failure for NiTi files than SS files [43]. • Reduced hardness and cutting efficiency compared to SS. • Undergoes cyclic fatigue as requires rotary use. • Incomplete debridement of all canal walls [28]. • Higher risk of perforations in inexperienced clinicians. • Unable to precurve files for ease of access due to shape memory effect[c]. • Reduced tactile feel [16,58–60].	Current instrument of choice for efficient and effective cleaning and shaping of the root canal space. Manual NiTi endodontic files are also used similarly to SS manual files.

[a] Highly variable between each manufacturer resulting in variations in mechanical and chemical properties [11,37].
[b] Glide path relates to maintenance of a pathway from canal opening to terminus using a size 10–15 SS K-file so subsequent engine driven instruments can follow. More recently, NiTi rotary files with small diameter tip have been designed to achieve the glide path [1].
[c] Newer rotary NiTi endodontic file systems have reduced shape memory effect to allow precurving into canals.

approximately 56% (wt.) nickel (Ni) and 44% (wt.) titanium (Ti). They demonstrate greater flexibility and elasticity allowing for instruments and preparations to better conform to the natural shape of the root canal, particularly in curved canals [18,26]. Whilst some deviations can be seen, NiTi instruments generally create a more centered canal preparation with reduced straightening effect, making them the instrument of choice for most clinicians [27–30]. However, with higher flexibility, less force is required to unwind these instruments and there is reduced cutting efficiency when compared to SS. With super-elasticity, there is also increased fatigue resistance [31–33]. This characteristic is attributed to the unique crystalline structure of NiTi alloy, allowing it to return to its original shape on unloading after significant deformation.

When endodontic files are used in rotation, they are subjected to tensile and compressive stresses, particularly in curved canals at the point of curvature [34]. This may lead to NiTi files to fracture, either through cyclic fatigue or torsional overloading [35]. Cyclic fatigue occurs when there is repeated extension and compression of the metal, causing work hardening and then fracture [36]. Torsional fracture occurs when excess pressure is placed apically on the file, wedging the file tip into the canal, and causing excess fraction and fracture [35].

Table 1 highlights the advantages and limitations of NiTi endodontic files compared to traditional SS endodontic files used in cleaning and shaping of the root canal system. Overall, NiTi allows for more centered preparations to maintain the original canal shape, reduced straightening effect and greater conservation of the dentin when preparing a diverse range of anatomical variations compared to SS.

2.1. Structure of NiTi

The unique mechanical properties of NiTi instruments (shape memory and super-elasticity) are a function of temperature and stress, and are a result of the transition from body-centric austenitic to martensitic monoclinic crystal structure [11]. When heated, NiTi is a body-centered cubic structure known as austenite or "parent phase" [12]. It displays high yield strength, modulus of elasticity and electric resistivity when cooled through a critical transformation temperature range (TTR). When cooled, there is linear thermal contraction until a limit is reached (martensite start; Ms), beyond this limit, contraction accelerates [61]. The shear transformation is progressive until a monoclinic structure is reached called martensite (martensite finish; Mf). Shape memory and super-elasticity is due to this change in crystal structure. When reheating the martensitic state, it will reverse this process, resulting in an austenite phase with similar austenite start (As) and finish (Af) points [12,25,62]. Fig. 2 is a diagrammatic representation of the shape memory effect of NiTi alloys.

When shear type force is applied or there is cooling prior to the completion of martensitic transformation, it is called the rhombohedral phase (R-phase). Contrary to its name, it gives rise to twinned martensite that resembles closely packed hexagonal lattice [61,63,64]. Even though there is no macroscopic change, when an external force is applied, it can deform readily into de-twinned martensite [65]. This can be reversed if heated above the TTR, allowing the NiTi to return to its original parent structure, body centered cubic lattice [11].

This ability is called shape memory. By forming strong, energetic, and directional electron bonds that pull displaced atoms back into its original position, it allows instantaneous transformation of the alloy into its previous shape.

2.1.1. Manufacture of nitinol instruments

Conventional SS files are produced by twisting wire blanks [66]. On the other hand, NiTi files are typically machined and not twisted, as the blank would return to its original shape on release of the applied twisting force [11]. More recent advancements in manufacturing processes have allowed the twisting of files into its desired shape [67]. When files are machined, the process promotes work hardening on the surface of endodontic instruments and creates surface defects [68]. When instruments are in use, R-phase transformation will occur in stressed file section, giving maximum strain in the direction of the applied stress [69]. It is likely through reorientation in stress reversal that defects gradually accumulate. Potentially, defects in the lattice created under high stress limit the transition of martensite into other phases [69].

The manufacturing process generates surface irregularities of varying extent on endodontic files [70]. These defects can influence fatigue resistance as failures can nucleate from the defect [71,72]. Crack nucleation occurs most of the time on the surface of the outer curvature in a curved canal. Whilst manufacture of defect-free endodontic files is feasible, exisiting defects do not affect the stability of NiTi files when in use [68,73]. In theory, the presence of surface defects and reduced microhardness of NiTi instruments (303–362 Vickers Hardness Number (VHN)) may compromise the cutting efficiency of NiTi when compared to SS (522–542 VHN) [74,75]. However, the difference in microhardness is negligible considering the VHN of sound human dentin is approximately 57–62 [76]. Pre- and post-manufacturing heat treatments and surface modifications have attempted to improve flexibility, increase cyclic fatigue resistance, or improve overall cutting efficiency. It is important to note that use of these strategies should not reduce the inherent super-elasticity and shape memory effect.

2.2. Thermomechanical treatment. Pre- and post-machining heat treatment of NiTi alloys

Traditional NiTi alloy instruments conventionally exist in the austenite phase at room and body temperature; however, this limits their use in severely curved canals due to their stiffness and low resistance to fatigue [77,78]. Heat treatment releases the internal strain of NiTi and increases the phase transformation resulting in more martensitic phase at clinically relevant temperatures potentially modifying the instrument's fatigue resistance (torsional or cyclic fatigue) [77,79,80].

NiTi particles are finely spread throughout the matrix [81], and two annealing temperatures can be differentiated. Temperature of approximately 600 °C demonstrated two-step transformations of austenite to R-phase to martensite, whereas over 600 °C there is direct martensitic transformation [69]. Application of heat treatment prior to machining could decrease the work hardening effect on the alloy inherent to the machining process of the file [68,69]. This results in NiTi files that have higher flexibility and fatigue resistance compared to conventional NiTi files. Table 2 summarizes the variety of pre- and post-machining properties of various heat treatment processes.

2.2.1. M-wire

To maintain NiTi alloy at a martensitic state at room temperature for better durability and flexibility, Tulsa Dental developed a thermomechanical process dubbed M-wire in 2007 [63,82]. The raw NiTi wire (containing 55.8 $\pm$ 1.5 wt% Ni, 44.2 $\pm$ 1.5 wt% Ti and trace elements less than 1 wt%) [82] is drawn in the martensitic phase to the final diameter and undergoes a series of heat treatment and annealing cycles under strain, before ground into the desired file shape [83,84].

The Af temperature of M-wire is around 43–50 °C which is higher than the Af of conventional NiTi and body temperature [63,84,85]. Consequently, M-wire contains a higher mix of crystalline states of deformed and micro-twinned martensite, R-phase, and austenite, compared to austenitic conventional NiTi [63,85,86]. The presence of more martensite allows M-wire to maintain a superelastic state.

Early studies on M-wire demonstrated significantly higher cyclic fatigue resistance compared to conventional NiTi alloys [83,87–89]. Greater fatigue resistance and flexibility was theorized to be due to higher transformation temperatures and greater presence of mixed martensitic phase, resulting in lower elastic modulus, smaller transformation stress and mechanical hysteresis [84]. However, other studies have found no difference in cyclic fatigue of M-wire and conventional NiTi files [90,91]. Perez-Higueras et al. [90], compared ProTaper Next

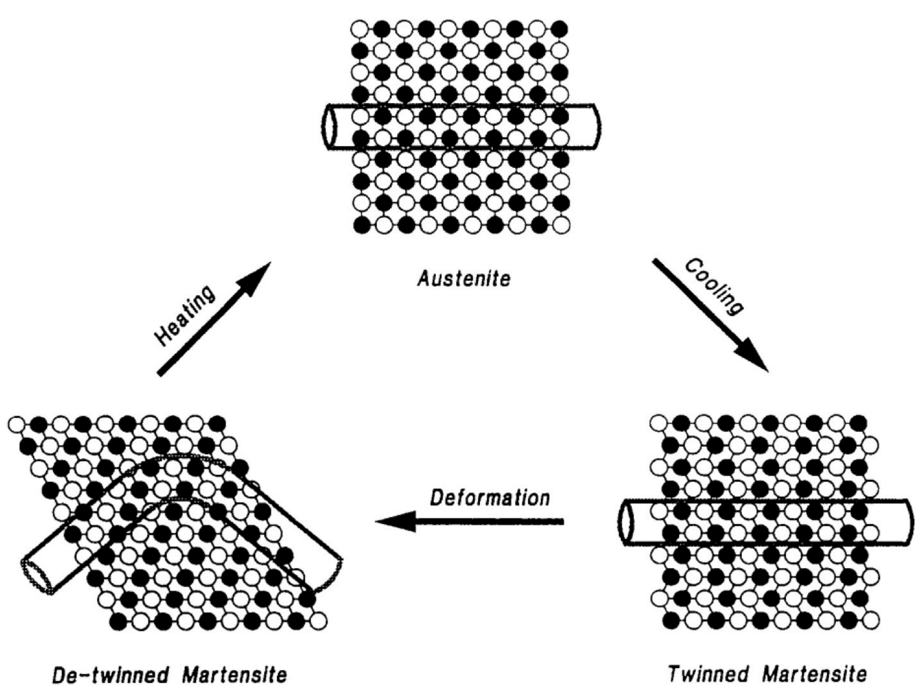

Fig. 2. Diagrammatic representation of the shape memory effect of NiTi alloy. Reprinted with permission from Thompson 2000 [11].

Table 2
Comparison of pre- and post-machining heat treatment properties for Nitinol.

Treatment Type	Fabrication	Properties	Advantages
M-Wire Pre-machining heat treatment Examples: Dentsply's ProFile GT Series X, ProFile Vortex, ProTaper Next, ProTaper Ultimate Slider, Path Files, WaveOne, and Reciproc (VDW, Munich, Germany)	• Raw NiTi wire is drawn in the martensitic phase to the final diameter and undergoes a series of heat treatment and annealing cycles under strain then ground into the desired file shape.	• Mainly austenitic phase with small amounts of R-phase and martensite • Superelastic • Undergoes two stage stress-induced transformation via R-phase	• Greater cyclic fatigue resistance
R-phase Combination of pre- and post-machining heat treatment Examples: Twisted File (TF), Twisted File Adaptive (TFA) (SybronEndo, Orange, CA, EUA), K3XF (SybronEndo, Orange, CA, EUA)	• TF and TFA: R-phase heat treatment, twisting of the raw metal wire and special surface conditioning. • K3XF: R-phase heat treatment, grinding of the file followed by additional heat treatment for stability.	• Austenitic phase; • Superelastic and flexible when under stress	• More centered preparations with less transportation compared to conventional NiTi. • Greater cyclic fatigue resistance
CM-wire Post-machining heat treatment Examples: Hyflex CM, Hyflex EDM (Coltene/Whaledent), THYPOON Infinite Flex (Clinician's Choice Dental Products), V-Taper 2H (SS White, Lakewood, NJ, US)	• Hyflex CM files are produced via grinding of the CM alloy. • Hyflex EDM files are manufactured using EDM technology • TYPHOON undergo controlled temperature transitions.	• Mainly stable martensite phase	• Reduced straightening effect • Improved flexibility and cyclic fatigue compared to M-wire and other conventional NiTi instruments.
Gold and Blue heat-treatment Proprietary thermomechanical treatments after grinding process, blue or gold colored surface layer. Examples: ProFile Vortex Blue; ProTaper Gold; WaveOne Gold; ProTaper Ultimate Shaper and Finishers (gold); ProTaper Ultimate Auxiliary Finishers (blue) (Dentsply), Reciproc Blue, (VDW); Genius Proflex (Medidenta, Nevada (NV), USA); X1 Blue (MK Life, Porto Alegre, Rio Grande do Sul, Brazil); Aurum Blue (Meta Biomed, Osong, Korea); Blueshaper (Zarc4Endo, Gijón, Spain); One Files Blue; Super Files Blue (Flydent, Shenzhen, China)	• All use M-wire as a basis. • Blue color: TiO_2 layer on surface. • Gold: Repeated heating and cooling of raw wire. • ProTaper Ultimate: Combination system including M-wire, Gold and Blue heat-treatment.	• Mainly stable martensite or R-phase	• Reduced overall microhardness with greater surface hardness. • Centered preparations. • Improved flexibility and cyclic fatigue compared to M-wire and other conventional NiTi instruments.
Cryogenic Treatment (CryoT) Not available in the market	• Wet CryoT • Dry CryoT	• Increased martensitic content	• Improves surface hardness and thermal stability • Improved cutting efficiency in dry CryoT technique
Recent Developments in Heat Treatments			
• TRUShape (Dentsply Tulsa Dental Specialties, Tulsa, OK, USA); TruNatomy (Dentsply Sirona, Ballaigues, Switzerland)	• Proprietary novel heat treatment technique	• R-phase and martensitic transformation temperatures overlap during cooling and heating cycles whereby the transformation temperatures cannot be clearly separated	• Improved preservation of dentin • Minimal canal transportation • Greater number of "touched" walls by the instrument • Improved flexibility
• MaxWire – XP-endo Finisher; XP-endo Shaper (FKG Dentaire, La Chaux-de-fonds, Switzerland)		• Martensitic at 20 °C and austenitic at 35 °C	
• T-wire – 2Shape (MicroMega, Besancon, France)		• Mostly martensitic with some austenite and R-phase presence	
• C-wire – OneCurve; RECI One (MicroMega, Besancon, France)		• Mostly martensitic with some austenite and R-phase presence	
• FireWire – EdgeOne Fire; EdgeSequel Sapphire; EdgeTaper Platinum; EdgeFile X7 (EdgeEndo, Johnson City, Tennessee, USA)		• Mostly martensitic with some austenite and R-phase presence	
• AF-R Wire – F-One; S-One (Fanta Dental Co., Ltd., Shanghai, China)		• Mostly martensitic with some austenite and R-phase presence	
• FKG heat treatment – R-motion file System; Race Evo (FKG Dentaire SA, La Chaux de Fonds, Switzerland)		• Phase transition ranging from 32 °C to 35 °C (between martensite and austenite)	
• ZenFlex (Kerr Corporation, Pomona, CA, USA)		• At room temperature it is mainly R-Phase and martensitic, whilst at body temperature it is mainly austenitic•	

(M-wire, Dentsply Sirona, Ballaigues, Switzerland) files against ProTaper Universal (Conventional NiTi, Dentsply Sirona) and found cyclic fatigue resistance was more associated with instrument diameter than their metallurgical properties. Gambarini et al. [91], found files produced with M-wire were no more resistant to fatigue than files made conventionally. Newer generations of heat treatment techniques have demonstrated greater stability of martensite than M-wire, increasing the softness, flexibility, and fatigue resistance of the endodontic files under clinical conditions [12,62,92].

Current clinical examples of pre-manufacture heat treatment M-wire endodontic files include ProFile GT Series X, ProFile Vortex (Dentsply Tulsa Dental, Tulsa, OK, United States of America (USA)), ProTaper Next, ProTaper Ultimate Slider, Path Files, WaveOne (Dentsply Sirona), and Reciproc (VDW GmbH, Munich, Germany).

2.2.2. R-phase

SybronEndo introduced a new manufacturing process by twisting raw NiTi wire from austenite to R-phase through a thermal process and marketed it as Twisted-File (TF) in 2008 (SybronEndo Orange, California (CA), USA). The manufacturer claims three design features of TF: R-phase heat treatment, twisting of the raw metal wire and special surface conditioning [93].

R-phase occurs at a very narrow temperature range between the austenitic and martensitic forms [11]. When compared to conventional NiTi files, they have increased resistance to cyclic fatigue and greater flexibility [67,91]. Through heating and cooling, the austenite phase is transformed to the R-phase crystalline structure. TF and Twisted-File Adaptive (TFA; SybronEndo) are the only file systems that are twisted into shape whilst in R-phase, before undergoing a series of heating and cooling to maintain its new shape and convert it back to austenitic crystal structure, it would be super-elastic when stressed [67,91]. The shear modulus of R-phase is less than one tenth of marteniste, this means that less stress is required to apply plastic deformation to R-phase [94]. The surface is then conditioned through a proprietary process called Deox [95], where surface oxide layer and impurities are removed without impacting on the base material to maintain its new shape by converting it back to austenitic phase [94]. This manufacturing process aims to maximize the strength in the grain structure as traditional grinding process creates micro-fracture points. This avoids the need for further finishing or polishing procedures which can dull the cutting edges and reduce cutting efficiency [91,96].

However, Larsen et al. [93] found that whilst TF appeared to have improved cyclic fatigue resistance compared to conventional NiTi, it did not demonstrate further benefits compared to other heat treated systems. In addition, the cross section, file diameter and rake angles can affect file flexibility and fatigue strength [90,93]. Park et al. [97] used a "torque-controlled" motor with an "auto-stop" function where once maximum torque was reached, the engine stopped automatically. They measured the number of load applications until torque fracture was achieved and found no additional benefit regarding torsional fracture when comparing TF with conventional NiTi files [97]. TF was also found to have significantly lower yield strength, ultimate strength and low toughness compared to other file systems [98].

K3XF (developed 2011, SybronEndo) also uses R-phase technology. They are manufactured using traditional grinding process with post-machining R-phase heat treatment, this was to modify the crystalline structure of the alloy to accommodate some of the internal stress caused by the grinding process [25]. Direct comparisons can be made between K3XF (R-phase) and K3 (conventional NiTi) as they have the same design features. K3XF demonstrated greater flexibility and resistance to cyclic fatigue compared to the original conventional K3 NiTi file [99,100], but maintained the same torsional properties [101].

Overall, R-phase heat treatments demonstrated improved flexibility and greater cyclic fatigue resistance when compared to conventional NiTi grinding methods. When compared to other heat treatment methods, there has been no additional benefits demonstrated and in some cases fare worse.

2.2.3. Controlled memory alloys

Controlled memory (CM) wire was introduced in 2010 [102] and is another example of post-machining heat treatment. CM-wire aims to further increase flexibility, reduce shape memory, and raises austenite finish temperature to about 50 °C and obtain a stable martensite at body temperature. CM-wire contains a lower percentage of Ni (52% wt.) compared with conventional NiTi alloy due to the proprietary thermo-mechanical processing of the NiTi wire [103]. CM-wire contains mainly stable martensite phase and does not have the superelastic properties of conventional NiTi, as the Af temperature is above body temperature [77]. This controlled memory effect allows the endodontic instrument to maintain the shape of the canal even when it has been removed from the canal, similar to Vortex Blue. Their original shape can be restored after heat application or autoclaving procedure. The extreme flexibility and less taper of the files allow for increase fatigue resistance in curved canals [104]. However, single use is recommended as there is an increased tendency of permanent plastic deformation during use.

HyFlex CM and HyFlex EDM (Coltene/Whaledent AG, Altstätten, Switzerland) are both made from CM-wire (commercialized in 2011). Hyflex CM (HCM) files are produced via grinding of the CM-wire whereas Hyflex EDM (HEDM) files are manufactured using EDM technology [105]. EDM is a "noncontact production method" that is used in manufacturing parts that are difficult to make via conventional methods [106]. An electric potential is built up between the workpiece and the tool to change the shape of the workpiece. Sparks are initiated that melt and vaporize the top layer of the workpiece. This creates the characteristic surface feature of regularly distributed craters [107].

HCM austenite finish temperature is 47–55 °C [77]. The manufacturer claims that HCM is up to 300% more resistant to cyclic fatigue compared to conventional files [108]. It has been demonstrated to have reduced canal straightening effect compared to certain files systems [109,110]. However, in the same studies, other files systems could not demonstrate the same effect [109,110]. CM-wires have increased flexibility compared to M-wire and other conventional NiTi instruments [64,111]. There is also increased lateral cutting efficiency when compared to conventional NiTi instruments, despite having greater flexibility [112]. It is speculated that as CM-wire is relatively soft and pliable, it can have higher and more even distribution of contact with the material resulting greater cutting ability.

Manufacturer claims HEDM is up to 700% more resistant to cyclic fatigue compared to HCM [107,108]. This is consistent with various studies that demonstrate HEDM displays significantly higher cyclic fatigue resistance when compared to M-wire [64,105,107]. Even though there is a higher amount of martensite and R-phase, HEDM exhibited higher hardness compared to HCM [113]. HEDM can also maintain centered preparations well, preserving the original root canal anatomy [114,115].

Another example of CM-wire is TYPHOON Infinite Flex, first introduced in 2011 (TYP; Clinician's Choice Dental Products, New Milford, Connecticut (CT), USA). They undergo special thermal processing that control the temperature transition and are characterized by austenite finishing temperature of approximately 55 °C. This results in a highly flexible instrument at room temperature, as the alloy would contain a significant proportion of martensite [77].

Other CM-wire examples include V-Taper 2H (SS White, Lakewood, New Jersey (NJ), USA) with reported similar results of significantly higher resistance to cyclic fatigue compared to M-wire and conventional NiTi instruments [64]. The main benefit of files with reduced shape memory is the ability to precurve the NiTi file prior to insertion of the file into the limited space within the root canal chamber. Combined with its increase flexibility, it is best suited for preparation of curved canals as they possess superior centering ability compared to conventional NiTi instruments. This minimizes the amount of tooth structure that is removed during the preparation process.

2.2.4. Gold and blue heat-treated instruments

More recently, special thermomechanical treatments after the grinding process have imparted a blue or gold coloured oxide layer on the surface of the instrument [62,116]. This introduced a range of file systems with a blue or gold hue. There is an increasing number of gold and blue-heat treated files introduced into the market. Examples of gold heat-treatment include ProTaper Gold; WaveOne Gold (reciprocating); ProTaper Ultimate Shapers and Finishers (Dentsply Sirona). Examples of blue heat-treatment include ProFile Vortex Blue; ProTaper Ultimate Auxiliary Finishers (Dentsply Sirona); Reciproc Blue (reciprocating) (VDW); X1 Blue (MK Life, Porto Alegre, Rio Grande do Sul, Brazil); Aurum Blue (Meta Biomed, Osong, Korea); Blueshaper (Zarc4Endo, Gijón, Spain); One Files Blue; Super Files Blue (Flydent, Shenzhen, China). These systems also allows the user to prebend instruments, displaying controlled memory effect [117], though they differ from CM-wire as the files are ground prior to post machining heat treatment [111].

Vortex Blue and Reciproc Blue are manufactured using M-wire as a basis, through a complex proprietary heating-cooling treatment, a distinctive blue colour is achieved due to the TiO_2 layer [117]. The transformation temperatures are generally lower compared to other instruments, where the austenite finish temperature for Vortex Blue is approximately body temperature (38 °C) and the martensite start temperature is at (31 °C) [118]. Blue heat treatment has lower microhardness, greater flexibility, and improved cyclic fatigue resistance [119, 120], which is attributed to the presence of more stable martensite particularly when compared to M-wire.

ProTaper Gold and WaveOne Gold are also manufactured using M-wire [62]. Its characteristic gold appearance is due to the unique heat treatment process where the raw wire is repeatedly heated and cooled. Similar to blue heat treatment, ProTaper Gold's phase transformation is above body temperature allowing it to maintain martensitic or R-phase when in clinical conditions [121]. Plotino et al. demonstrated ProTaper Gold had higher resistance to cyclic fatigue compared to its predecessor made from M-wire alone [122].

Gold and blue heat-treated files present with improved flexibility and resistance to cyclic fatigue when compared to conventional NiTi and M-wire instruments [12,79,117,119,121–128]. Hyflex EDM files are the only system that have been found to have significantly greater cyclic fatigue resistance compared to gold and blue treated files [126,129]. The gold and blue heat-treated files have consistently created well centred preparations in canals with severe curvatures [114,130,131]. However, more recently, studies have found blue heat treatment either does not reduce transportation and, in some instances, causes more canal transportation [132,133]. Finally, gold and blue heat-treated instruments result in a harder surface layer that compensates for the reduced overall microhardness [119], this possibly explains the increased effectiveness of ProTaper Gold when used with a lateral cutting action [134].

Since the first introduction of gold and blue heat-treatment into endodontics by Dentsply Sirona Endodontics and VDW, many other companies have introduced “replica-like” files that have undergone similar heat-treatments to imbue the gold/blue hue on their endodontic files [135–137]. Examples of these include Premium Taper Gold (Waldent, New Delhi, India), Go-Taper Flex (Access, Shenzhen, China), BlueShaper (Zarc4Endo, Gijón, Spain), Super Files Blue and One Files Blue (Flydent, Shenzhen, China). Currently, there is limited independent literature that describes their clinical and mechanical performance, efficacy, and safety.

Martins et al. [136–138] demonstrated that replica-like files had equiatomic ratio of Ni to Ti as compared to their respective original brand instrument, and differential scanning calorimetry (DSC) analysis often showed differences in the phase transformation temperatures amongst original and replica file systems. Reciproc Blue (VDW) and WaveOne Gold (Dentsply Sirona) have martensitic characteristics with R-phase finish (Rf) temperatures at 20.7 °C and 29.6 °C, respectively [137]. Alternatively, One Files Blue had a higher Rf temperature of 33.3 °C. This influences its mechanical performance, for instance, One Files Blue has greater cyclic fatigue strength correlating with the higher martensitic composition due to higher R-phase start (Rs) temperatures. However, even with the higher martensitic content, it was significantly less flexible as compared to Reciproc Blue, which may be explained by the larger metal core of One Files Blue [137]. Until there is an established standard on the minimum quality of NiTi instruments prior to being marketed, the clinician should be cautious when selecting endodontic NiTi files that are not from the well-known brands as their performance may differ compared to well researched systems [139].

2.2.5. *Cryogenic treatment (CryoT)*

A reduced temperature environment has been used to treat NiTi alloys during the manufacturing process to improve surface hardness and thermal stability [140,141]. Wet CryoT involves submersing metal in a super cooled liquid nitrogen (N) bath (−125 °C to −196 °C) and then allowing the metal to warm slowly to room temperature [140–142]. On the other hand, dry CryoT is when the file is held above the level of the liquid N and evaporating vapors from cryogenic liquid are used to cool the files. Dry CryoT allows for gradual change in temperature to avoid thermal shock that would make the instrument brittle [143]. CryoT is inexpensive and affects the bulk of the material rather than just the surface [142].

NiTi alloy martensitic transformation temperature occurs below room temperature. This allows CryoT to potentially influence the stress-induced martensitic transformation and increase the martensite content of NiTi alloys [144].

Measuring the microhardness at the cutting edge of the file, Kim et al. [38] immersed NiTi files in liquid nitrogen at −196 °C and found the mean microhardness increased from 339.3 VHN to 346.7 VHN after wet CryoT. When there is increased hardness, it generally also correspond to an increase in wear resistance for most materials [145]. This in turn should increase cutting efficiency. However, Kim et al. did not find any clinically detectable increase in cutting efficiency or change in crystalline phase composition [38]. It is important to note that the cutting efficiency in this study was a subjective measure of what the observers felt had cut more efficiently.

Vinothkumar et al. [143] on the other hand found cutting efficiency was significantly increased without affecting the wear resistance of cryogenically treated NiTi files, likely related the use of dry CryoT technique.

Using a dynamic cyclic axial motion to mimic the brushing and pecking action in clinical practice, George et al. [146] found that dry CryoT improved cyclic fatigue resistance. Similarly, Vinothkumar et al. [147] demonstrated that dry CryoT drastically increased the cyclic fatigue resistance by 13%. This contrasts with more recent studies that found no improvement in cyclic fatigue resistance in NiTi rotary instruments after cryogenic treatment [148,149]. Differences in methodology likely explains the contrasting results. Yazdizadeh et al. [149] and Sabet et al. [148] used a wet CryoT technique and measured cyclic fatigue using a static model which is not reflective of clinical practice.

2.2.6. *Recent developments in heat treatments*

There is ongoing development in heat treatment technology and new endodontic file systems are continuously released into the market [65]. However, due to proprietary manufacturing processes, very little details on the heat treatments used are released. There is limited to information on transformation temperatures, phase composition and flexibility of these instruments.

TRUShape (Dentsply Tulsa Dental Specialties, Tulsa, Oklahoma (OK), USA) involves heat treatment applied after machining of flutes from NiTi file blanks with characteristic S-curve bends [150]. TRUShape have classic R-phase transformations, however, the R-phase and martensitic transformation temperatures overlap on cooling and heating cycles such that they cannot be clearly separated and defined [151]. It is well documented in the literature that instruments with larger inner core diameters have lower cyclic fatigue but better torsional resistance [97, 152–156]. This explains the lower cyclic fatigue resistance of TRUShape (0.06 taper) compared to HCM, K3XF and Vortex Blue (0.04 taper) [151, 157,158]. Though conflicting literature found the fatigue resistance of TRUShape was superior to Vortex Blue in double curvature canals [159]. TRUShape and ProTaper Gold had comparable surface microhardness [160] and TRUShape had no statistically significant difference in shaping capability or canal transportation when compared to M-wire [161].

TruNatomy (TN; Dentsply Sirona, Ballaigues, Switzerland) instruments are manufactured with proprietary post-machining heat treatment process. This increases its super-elastic properties and has reduced shape memory compared to conventional NiTi or M-wire [162]. TN demonstrated higher cycles to failure in single and double curved canals compared to VortexBlue [163], which may be due to greater austenitic content in VortexBlue at body temperature [157]. However, when using dynamic cyclic fatigue test with axial movements, Vortex Blue and HCM had greater number of cycles to failure [164]. When compared to ProTaper Gold and HEDM, TN had the least amount of canal transportation with greater potential to preserve tooth structure [165].

FKG Dentaire introduced MaxWire (Martensite-Austenite-electro-polish-fileX) that according to the manufacturer combined both shape memory and superelasticity [166]. There are currently only two instruments made of MaxWire; XP-endo Finisher and XP-endo Shaper (FKG Dentaire, La Chaux-de-fonds, Switzerland). Max-Wire instruments remain relatively straight at room temperature as they are predominantly martensitic, they undergo austenitic changes to a predetermined curved shape when exposed to intracanal temperatures. It is claimed that the curved shape allows for preparation of complex root canal geometries and irregularities [12]. XP-endo Shaper demonstrates significantly increased resistance to cyclic fatigue but reduced torsional resistance compared to other heat-treated NiTi instruments (TRUShape, HCM, Vortex Blue) [158,167,168], likely due to its narrow taper of 0.01 [97,152–156]. It is difficult to make any direct comparisons of any file against XP-endo Shaper as even though it has an initial taper of 0.01, when in use, according to the manufacturer, it expands insider the canal achieving a taper of at least 0.04 [166].

2Shape introduced T-wire technology (MicroMega, Besancon, France), and the manufacturer claims that the proprietary heat treatment process increases the instrument's resistance to fracture and increases the flexibility for better negotiation of curvatures [169]. Limited literature has confirmed this, when comparing T-wire heat treatment with conventional NiTi, T-wire improved cyclic fatigue limit, lowered bending stiffness without affecting torsional properties [170].

C-wire is a patented heat treatment developed for OneCurve and One Reci (MicroMega, Besançon, France) [171,172]. It is predominantly martensitic phase at room temperature and a mix of martensite and austenite at body temperature [173]. This allows the file the ability to pre-bent for ease of access into the root anal system [171]. It renders a golden layer of TiO_2 on the surface of the file and a greater resistance to cyclic fatigue compared to conventional NiTi files [174].

FireWire (EdgeEndo, Johnson City, Tennessee (TN), USA) is a mixed austenitic plus R-phase at room temperature and reported to have similar torque resistance as M-wire instruments with greater angles of rotation possibly due to a smoother surface finish [175]. There is increased cyclic fatigue resistance and undergoes plastic deformation when torsional stress is applied and required more energy to fracture [176–178].

AF-R wire is a proprietary heat treatment developed by Fanta Dental Co., Ltd (Shanghai, China). The manufacturer claims that AF-R wire has 600% higher resistance to cyclic fatigue compared to normal NiTi wire, improved cutting efficiency whilst preserving more dentin [179].

Manufacturer FKG have also introduced proprietary heat treatment to their new file systems RACE EVO and R-motion (FKG Dentaire SA, La Chaux-de-Fonds, Switzerland). FKG Dentaire claims these files offer greater resistance to cyclic fatigue, higher flexibility, improved cutting efficiency, lower stress on dentin and lower screwing effect [180,181]. Whilst the specific manufacturing process is unknown, the blue hue suggests a titanium oxide layer that is likely to enhance their resistance [182].

ZenFlex (Kerr Corporation, Pomona, CA, USA) claims to have greater resistance to cyclic fatigue when compared to VortexBlue with increased resistance to torsional stresses [183]. However, this is contradicted by Zanza et al. that demonstrated that ZenFlex had lower number of cycles to failure compared to VortexBlue, which may be due to more austenitic phase at room temperature in ZenFlex compared to VortexBlue [184].

Finally, Pink alloy has been introduced by Zarc4endo (Gijón, Spain), the manufacturer claims it provides sufficient torsional resistance to advance the file into very narrow or calcified canals [185]. There is no information or literature to support the claims from the manufacturer.

Overall, heat treatments allow for greater martensitic or R-phase to be present whilst in use within the canal system. Martensitic instruments are more flexible and are able to resist cyclic fatigue to a greater degree than conventional NiTi alloys. This is of greater benefit particularly when negotiating complex curvatures and root canal morphologies. It is important for the clinician to choose more martensitic instruments when attempting to negotiate these complexities as it prevents iatrogenic errors and allows the file to be precurved to access difficult canals in teeth. However, it is important to develop standardizations in research methodologies for comprehensive metallurgical and mechanical behavior of NiTi rotary instruments to obtain significant comparisons between various heat treatments [139].

2.3. Surface modification of NiTi alloy

Based on the inherent defects resulting from manufacturing process of NiTi instruments [68], attempts have been made to enhance its surface characteristics. Various surface modifications have been utilized to reduce or eliminate defects, improve hardness or flexibility, increase resistance to cyclic fatigue and enhance cutting efficiency. Following strategies have been employed to impart favorable characteristics to NiTi alloys for optimum performance as an endodontic file. Table 3 highlights key papers on surface modifications detailed in this section.

As such, surface modifications were explored to mitigate material-associated issues with NiTi alloy and instrument manufacture, such as low cutting efficiency and defect-induced fatigue failure. It is tempting however, to modify the surface to enhance clinical functionality., similar to what has been explored in intravascular stents (see Section 3 below).

2.3.1. Ion implantation

Ion implantation involves bombardment of voltage-accelerated ionized gaseous atoms where the ions become buried under the substrate surface. The depth depends on the accelerating voltage. The final result leaves a track of dislocations that enhance the toughness of the material [186].

Nitrogen (N_2) ion implantation increases wear resistance, cutting efficiency, and cyclic fatigue resistance, however, reduces hardness [187–190]. Wolle et al. [186] investigated the influence of N_2 and argon (Ar) ion implantation on the file morphology. The studies revealed how cracks could potentially develop and propagate, and their ability to resist cyclic fatigue. They found instruments implanted with argon could bear more fatigue cycles before fracture compared to endodontic files without any modifications, whereas N_2^+ implanted files had the worst performance in the fatigue test, only achieving around half the mean cycles to fracture. However, this study did not find significant crack formation and propagation, which is in contrast with results from Rapisarda et al. that demonstrated increase in wear resistance in files implanted with N ions [189]. This may be due to N having a higher atomic mass reducing formation of point defects in the crystalline structure. Also N reacts with Ti within the rotary endodontic file to form the very hard titanium nitride that may deter microfractures [189]. Clinically, increase in wear resistance could potentially increase the life of the instrument, whereby maintaining its precision and shape of blades after use and reducing the risk of instrument fracture.

Lee et al. used a high concentration of boron ions and implanted into NiTi alloys via a nonequilibrium process to successfully improve the surface hardness [191]. Boron was used instead of nitrogen as titanium-boron has better mechanical strength compared to titanium-nitride. This study used a flat polycrystalline NiTi alloy substrate and not an endodontic file, limiting the clinical translation of the results.

Plasma immersion ion implantation (PIII) was first introduced in the late 1980s by Conrad et al. [192] and Tendys et al. [193]. The specimen is placed in a chamber and immersed in plasma ion. A high negative pulsating voltage is applied where the ions are then extracted from the plasma, accelerated, and bombarded on to the surface of the specimen. This technique has been shown only to modify surface characteristics by forming a titanium nitride (TiN) layer resulting in a golden appearance. This improves the wear resistance without affecting the inherent

Table 3
Summary of various surface modifications of NiTi alloy surfaces.

Treatment	Author, Year	Key Findings
Ion implantation	Wolle et al., 2009 [186]	Ar implantation increased number of cycles before fractures whereas nitrogen implantation performed the worst on fatigue testing.
	Rapisarda et al., 2001 [189]	Increase in wear resistance after nitrogen implantation.
	Lee et al., 1996 [191].	Titanium-boron had improved mechanical strength compared to titanium-nitride.
	Li et al., 2007; Alves et al., 2014 [194, 195].	Plasma immersion ion implantation resulted in a golden surface layer of titanium-nitride that improved wear resistance.
Thermal nitridation	Rapisarda et al., 2000 [190]	Improved cutting efficiency however not great improvement compared to ion implantation.
	Shenhar et al., 2000; Huang et al.. 2005 [227,228]	Improved corrosion resistance.
	Lin et al., 2008 [196]	Formation of significantly increased corrosion resistance when in contact with 5.25% NaOCl.
	Li et al., 2006 [197]	Increase in cutting efficiency and corrosion resistance with NaOCl.
Electropolishing	Bonaccorso et al., 2008 [207]	electropolished files required a higher potential for pitting to occur suggesting increased resistance to corrosion.
	Cheung et al., 2007; Peters et al., 2007 [205,206]	Presence of corrosion pit whist associated with crack initiation, did not improve corrosion resistance. No difference in corrosion patterns detected.
	Tripi et al., 2006 [204]	Improved fatigue resistance in electropolished files compared to non-electropolished files.
	Herold et al., 2007 [208]	Electropolishing did not inhibit the development of microfractures on files.
	Bui et al., 2008 [215]	Significant reduction in cyclic fatigue resistance after electropolishing files.
	Kaul et al., 2014 [209]	Electropolishing removed all manufacturing defects however surface became weaker and more prone for crack formation.
Physical Vapor Deposition (PVD)	Schäfer, 2002 [220]	PVD increased in cutting efficiency compared to uncoated files.
	Chi et al., 2017 [222].	PVD increased cyclic fatigue resistance compared to untreated files
	Bonaccorso et al. 2008 [207]	PVD increased resistance to putting when immersed in sodium chloride.

microstructure and flexibility [194,195].

2.3.2. Thermal nitridation

In pursuit of improvements in surface hardness and wear resistance, another technique to produce a hard surface coating is thermal nitridation. The sample undergoes thermal processing in a N environment usually at high temperatures (200 °C–500 °C) [190,196], which creates a layer of TiN on the surface of the NiTi files. Rapisarda et al. [190] compared two different types of surface treatments involving TiN, ion implantation and thermal nitridation. Both techniques showed an increase in TiN presence compared to unmodified files and ion implantation showed a higher ratio of nitrogen to titanium. Both strategies had increased cutting ability compared to no surface treatment, though compared to thermal nitridation, ion implantation had higher cutting efficiency [190]. Lin et al. [196] demonstrated the presence of TiN on NiTi endodontic files significantly increased corrosion resistance when in contact with 5.25% NaOCl. Nitriding temperatures at 300 °C provided the highest corrosion resistance; however, there was a loss of NiTi superelastic properties after treatment. Therefore, nitriding temperature of 250 °C was recommended for clinical use [196]. Li et al. [197] also examined thermal nitridation at various temperatures and found increase in cutting efficiency and resistance to corrosion when in contact with NaOCl.

Another method of producing a layer of TiN is powder immersion reaction assisted coating (PIRAC). Substrates are annealed at high temperatures (from 800 °C to 1100 °C) in a sealed steel foil containers at low pressure [198,199]. Diffusion of highly reactive monatomic N_2 results in the formation of a nitrogen-rich layer on the surface of the sample that is highly uniform with a thin outer layer of TiN and a thicker layer of Ti_2Ni [200]. It is noteworthy that PIRAC coatings are similar to oxide films on NiTi alloys and have a strong adhesion to the substrate. However, this technique has been used on biomedical NiTi alloys but has not been investigated specifically on the NiTi endodontic files.

2.3.3. Electropolishing

Electropolishing is an electrochemical process that removes surface irregularities [21], as seen in Fig. 3. The file (anode) is placed in a temperature-controlled bath of electrolytes with a cathode, a direct current (DC) passes through the solution resulting in the dissolution of the anode into the bath [61]. A surface oxide layer is formed that acts as a protective film reducing surface residual stress, improve cyclic fatigue resistance and corrosion resistance [66,68,201–203].

Evidence to demonstrate that electropolishing improves corrosion resistance and fatigue life of NiTi files remains controversial. There is consensus that electropolishing enhances the surface smoothness of the endodontic file [204–209]. Electropolished files require a higher potential for pitting to occur compared to non-electropolished files, indicating increased resistance to corrosion [207]. Other studies have found whilst the presence of a corrosion pit was associated with crack initiation, electropolishing did not improve the resistance of corrosion [205, 206].

Enhanced cyclic fatigue resistance after electropolishing has been demonstrated in multiple studies [201,204,210–213]. It is hypothesized that surface irregularities would serve as points for stress concentration and result in crack initiation [201], where larger groove defects would result in reduced number of cycles until fracture [214].

On the other hand, Herold et al. [208] found electropolishing (EndoSequence) did not inhibit the development of microfractures when examined under SEM, in comparison with conventional untreated ProFiles. Bui et al. [215] on the other hand, found significant reduction in resistance to cyclic fatigue in experimental electropolished Profiles compared to conventional ProFiles in simulated canals in plastic blocks. Higher maximum torque values were required when using electropolished files [216], implying that electropolishing may level and blunt the cutting edges thus needing higher torque to achieve the same level of preparation. When examined, crack lines were not always consistent with the machined grooves [217]. Kaul et al. [209] found whilst electropolishing removed all manufacturing defects, the resulting surface was weaker and more prone to formation of new cracks. Overall various other studies found electropolished files did not demonstrate greater resistance to cyclic fatigue compared to any other file systems being tested [93,218]. Limited effect on cutting efficiency and torsional resistance was found with electropolishing [201,210,215]. In summary, electropolishing creates a smoother finish on endodontic files, however, there is conflicting research to suggest any benefits of this surface treatment.

2.3.4. Physical or chemical vapor deposition

Physical Vapor Deposition (PVD) have been used to coat medical devices since the late 1980s to improve wear resistance [219]. Currently there are three main forms of PVD technology: ion plating, magnetron sputtering and arc evaporation [220]. PVD creates a dense and uniform film layer that has excellent corrosion resistance, improved surface hardness, and has good biocompatibility [220]. For the optimum

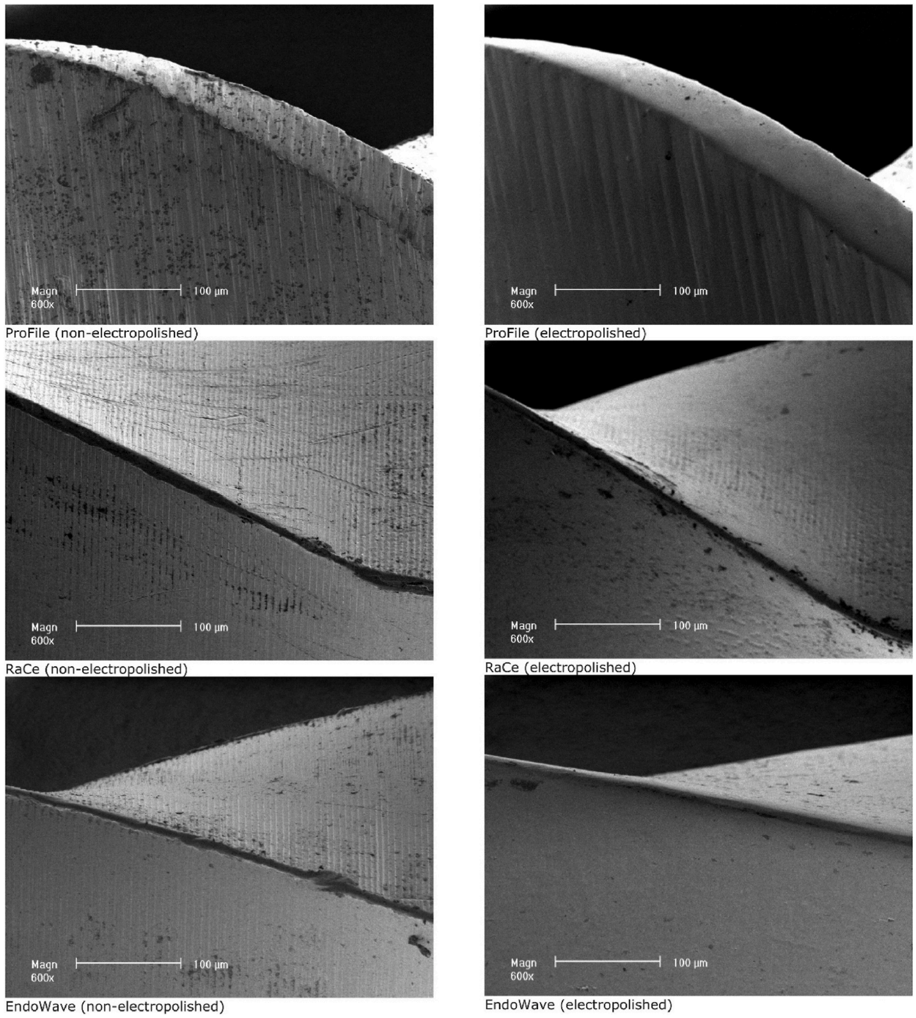

Fig. 3. SEM images of electropolished and non-electropolished endodontic instruments (ProFile (Dentsply Sirona), RaCe (FKG) and EndoWave (J Morita Corporation, Osaka, Japan)). Reprinted with permission from Anderson et al. 2007 [201].

adhesion of the coating to the metal surface, cathodic arc evaporation technique is commonly used. This creates hard coatings of TiN, titanium carbide (TiC), titanium-carbon-nitride (TiCN), and titanium aluminum nitride (TiAlN). Through this technique, a fine grain TiN film layer is deposited on the surface of files at low temperatures. This TiN film can improve cutting efficiency, surface hardness and wear resistance [189,190]. When the coating thickness is around 1–7 μm, the surface hardness can be up to 2200 VHD. By creating a continuous amorphous layer on the surface of the file, surface irregularities, cracks and potential residual stresses are removed, improving the longevity of the endodontic instrument [71,221].

Schäfer first demonstrated the application of PVD on NiTi K files and found up to 26.2% increase in cutting efficiency compared to uncoated instruments [220]. Chi et al. used PVD to add a novel surface layer of Ti-Zirconium–Boron film which presented a very smooth file morphology and exhibited higher cyclic fatigue resistance compared to untreated files [222]. Bonaccorso et al. [207] demonstrated increased corrosion resistance in PVD instruments. The study found greater pitting resistance of PVD files compared to electropolished or non-electropolished file when immersed in sodium chloride solution for 1.5 h. The results of this study cannot be readily transferred to clinical situation as endodontic procedures do not commonly use sodium chloride solutions. However, Qaed et al. [223], found that electropolished files had better performance than PVD files.

Chemical vapor deposition (CVD) similarly deposits a surface layer of TiN at high temperatures of 300 °C [224,225]. Early studies demonstrated that metal organic CVD was the preferred method and can increase the Ni:Ti ratio up to two times on the surface of the substrate [225]. However, whilst both PVD and CVD can add a hard surface coating on NiTi instruments, CVD results in continuous layers of amorphous materials with poor crystalline structure, whereas PVD deposited films of well-defined grains [224].

It is noteworthy that the surface coating may be exposed as the cutting edges of the file wears down [220], and the fragments can potentially become lodged within the canal space. Release of such metal ions or nanoparticles can result in toxicity [226].

Overall, there have been controversies on the application of static versus dynamic file testing and its relevance to clinical endodontics [229]. Static tests often involve either bending the file until fracture or allowing it to rotate freely in a straight or curved canal until fracture [34]. Dynamic testing introduces vertical and/or lateral movements at the same time [230]. It has been suggested that dynamic movements of the file better simulate the stress that is generated on a file in clinical application compared to static tests [230]. Static tests on the other hand, can only make comparisons of instruments of a defined size and used in a root canal with identical length, curvature, and diameter. Zanza et al. provides an updated review on NiTi endodontic instruments discussing in detail the current limitations of static tests and how the combination of flexural and torsional stresses impact root canal instrumentation [65]. Considering the great variation in instrument geometry, cross section, taper, etc. between different companies and manufacturers, until there are standardizations of static and dynamic testing, it is difficult to make satisfactory comparisons between instruments.

3. Surface functionalization of NiTi endodontic files

Surface functionalization overall aims to induce a desired bio-response or inhibit a potentially adverse reaction. Within orthodontics, surface roughness is crucial in determining the efficiency of archwire-guided tooth movement [231]. Various coatings have been applied to reinforce this mechanical property [232]. Early coatings of polyethylene and Teflon coatings have been found to improve corrosion resistance and bracket-archwire friction [233]. Other surface coatings such as epoxy resin or low reflectivity rhodium coatings have been applied. These coatings can improve aesthetics [234], or reduce surface roughness and thereby improve oral hygiene by reducing the plaque accumulation compared to uncoated NiTi wires [235]. However, these coatings have been routinely found to be damaged after mastication and enzymatic activity in the oral cavity [236]. This would potentially allow for corrosive process to take place in the exposed regions and also cause significant plaque accumulation in the surface defects [237]. Damages in surface structure could be detrimental in the endodontic setting as fractured surface coating fragments might be dislodged within the root canal space and displaced outside of the root into the periapical area, with the potential risk of a foreign body reaction [238].

The majority of studies in endodontics relating to surface modifications has focused mainly on the shape and geometry made by these instruments, such as taper, conicity and ability to maintain the original canal position and their mechanical properties such as metallurgy, flexibility, torsion fatigue, cyclic fatigue, cutting efficiencies etc. So far only one study examines the possibility of adding a new function to endodontic instruments beyond its current ability to remove debris and shape the canal space. Cora et al. [239] investigated the antibacterial effectiveness of NiTi rotary files after application of a surface silver ion coating. Twenty-four NiTi ProTaper Universal endodontic files were coated with a silane-based, silver-complex solution (2% silver ion coating), using the dip-coating method at 25 or 50 mm/min [239]. The antimicrobial activity was evaluated against *Enterococcus faecalis (E. faecalis)*. Sample cultures were taken and incubated for growth and any growing bacterial colonies were counted. Cutting efficiency of the coated vs uncoated files was measured based on amount of debris lost in transparent resin blocks after preparation of an artificial root canal [239]. They also analyzed the files under SEM and SEM-energy-dispersive x-ray spectroscopy and found that silver ion surface coating was effective against *E. faecalis* and did not impact on cutting efficiency of NiTi rotary endodontic files [239]. This introduces the concept and possibility of added functionalization of NiTi rotary files.

4. Nano-engineered NiTi alloy

Nano-engineering of the surface of NiTi endodontic files have yet to be explored. It has been demonstrated that Ti and zirconia-based orthopedic and dental implants via various physical, chemical, biological and therapeutic modifications have enabled enhanced bioactivity and biofunctionality [219,240–242]. Among these electrochemical anodization stands out, attributed to its scalability and cost-effectiveness that enables controlled fabrication of metal oxide nanostructures on metallic implants [243,244]. This technique is used to fabricate an oxide layer with various nanostructure configurations [245]. Briefly, anodization involves immersion of metal implant as anode and counter electrode (cathode) in an electrolyte containing water/fluoride and supply of appropriate voltage/current [246,247]. Under specific anodization conditions (water/fluoride content, voltage, current, time, etc.), self-ordering of nanotopography (nanotubes (NT), nanopores (NP), nanospindles (NS)) occurs on the substrate/metal alloy surface [240, 243,248–251]. These topographical changes of the substrate surface have the potential to allow for additional functional abilities whilst still maintaining existing physical and mechanical properties without the use of surface coatings that generally have weaker bond strengths. A typical anodization setup to fabricate nanotubes on Nitinol is presented in Fig. 4.

NiTi alloy anodization dates back to 1980s, however this material has not been commonly used in biomedical applications until the twenty-first century [251]. It is an electrochemical process where elements of the alloy are oxidized by an electrical field whereby unoxidized sublayers such as Ni-rich layers in NiTi are eliminated after thermal oxidation [252]. Kim et al., first reported generation of Ni–Ti oxide NT using a ethylene glycol electrolyte base containing water (H_2O) and ammonium fluoride (NH_4F) [253]. They found that the NT could potentially perform well after as electrode materials in pseudocapacitors. It has since been investigated in biomedical engineering [251,254, 255] and areas outside of medicine such as gas sensing [256,257], biosensing [258], and electrochemical energy storage [259,260].

Application of appropriate voltage to electrochemical cell containing NiTi alloy anode, yields mixed oxide products of Ni and Ti. It is noteworthy that anodization of NiTi is more sensitive to electrolyte composition compared to other metals and their alloys, due to the presence of a large concentration of Ni [251]. Nickel oxide (NiO) is more susceptive to chemical etching compared to TiO_2, therefore there is preferential dissolution of NiO [21,251]. This results in a thick, uniform and homogenous film composed of titanium dioxide.

Modifications of various parameters involved in the manufacturing process such as voltage, electrolyte composition and time, can affect the precise dimensions and shape of the nanostructures [261]. Hang et al. extensively examined the impact of these parameters on nanotubule growth in NiTi alloys [258]. Changes in voltage resulted in a linear increase in the NT diameter and length up until 25V, where higher voltages resulted in the diameter remaining relatively the same or micropitting to occur. Higher electrolyte temperatures would increase the NT diameter initially then decrease when the temperature exceeding 30 °C, however this variation was quite minimal. The length of the NT would decrease as temperature increased from 10 °C to 50 °C. The longer duration of anodization would rapidly increase the NT length, however, after approximately 60min, they found the length remained at a steady state at 1100 nm. The overall length of NT is determined by growth and dissolution rates of the oxide formed, as the available fluoride (F^-) at the electrolyte/oxide interface is equal to the etching rate of the F^- at the base of the NT [262]. Finally, excess and inadequate amounts of H_2O content resulted in irregular porous structure. It is important to note that when the dissolved Ni concentration reaches a threshold, the conditions for growth of NT is halted [251].

Changing the electrolyte from F^- containing to chloride (Cl^-) containing allows the fabrication of NP instead of NT [263]. Hang et al., demonstrated under optimal conditions, ordered NPs can be fabricated up to 160 μm in length [263–265]. Irregular NPs are formed at lower concentrations of hydrochloric acid (HCl), ordered and straight NPs with increasing lengths can be seen when HCl concentrations increase from 0.125 M to 0.75 M [263]. Water content is also crucial to anodic growth as it is the source of oxygen in formation of the oxide layer [266]. Water content between 5.0 vol% and 11.0 vol% forms NPs and its length increases with increasing amount of water, however, too much can result in irregular structure [263]. Sufficient voltage is required for NP formation, too little will be insufficient to drive the oxidation and migration of chloride ions however too much results in excess etching of the Cl^- layer limiting the NP length achieved. Typical nanotubular arrays fabricated on NiTi wires are presented in Fig. 5 [267].

Hydrothermal treatment can transform NPs to crystallized NSs [250, 268]. When the hydrothermal treatment temperature was increased to 200 °C the NP structure was replaced with random arrangement of NS. The NS length was around 70–110 nm and diameter 16–24 nm. Extension of the time only slightly increased the dimensions of the NSs.

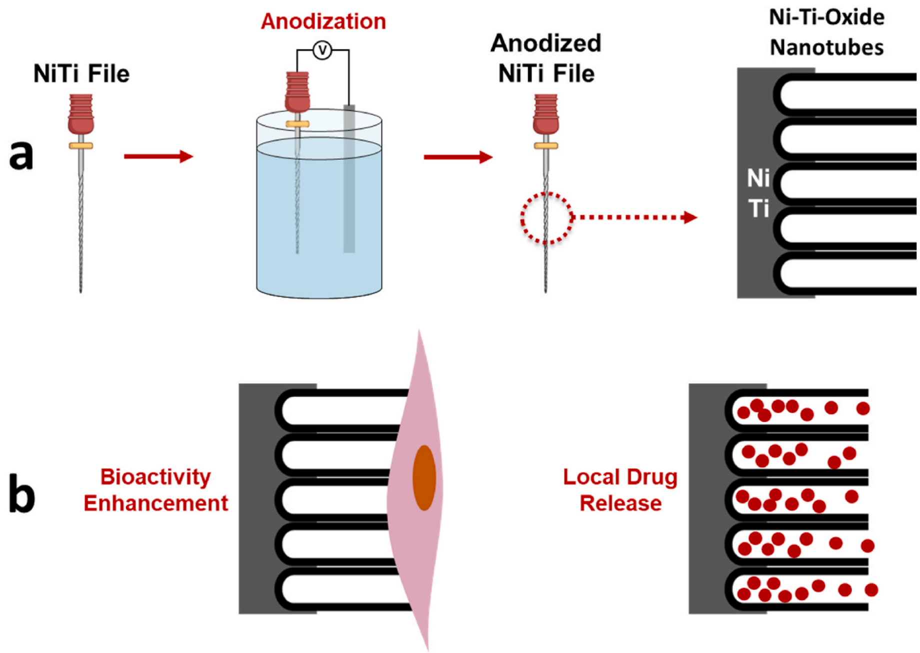

Fig. 4. Electrochemically anodized Nitinol. Schematic representation of (A) anodization setup to fabricate nanotubes on Nitinol file; and (B) bioactivity and local therapy applications (Color image).

Within the biomedical field, nanostructures formed on NiTi alloy surface have mainly focused on its interactions with various cell types and functions [255]. For example, cell proliferation rate, protein release, adhesive properties, gene expression, drug release etc. Lee et al. found human aortic smooth muscle cells had significantly decreased proliferation and migration rate on nanotubular surfaces [267,269]. The reduction of extracellular matrix proteins produced by the human aortic smooth muscle cells reflect its positive effect on preventing restenosis in implanted NiTi stents.

Local drug-delivery strategies have been investigated whereby NT act as drug reservoirs on Ti [270–273], and recent reports demonstrate drug impregnation techniques in NTs grown on NiTi alloys as well [274, 275]. As one of the main complications with drug-loaded NT is controlling the release of the therapeutic load from the NT, as sudden release can cause local toxicity and can re-trigger bacterial infection (in case of antibiotic release) [276]. Davoodian et al. applied a biodegradable polymer coating consisting of poly(lactic-co-glycolic acid) (PLGA) to modulate antibiotic release in NTs grown on NiTi discs [274]. It was found that coated NT's can modulate the drug-delivery kinetics and reduce the initial burst release and prolong the total release time of the

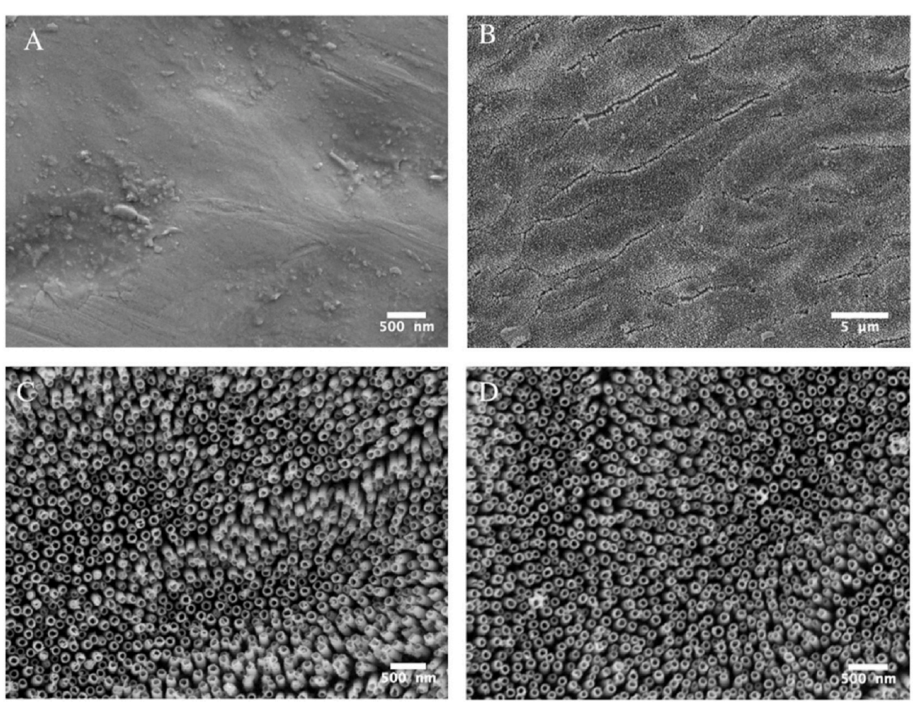

Fig. 5. Top-view SEM images of anodized Nitinol with nanotubes: (A) flat control Nitinol; (B,C) anodized at 85V and (D) 70V. Adapted with permission from Lee et al. 2014 [267].

therapeutic antibiotic dose. Other potential therapeutic agents can also be utilized for loading and local release, including growth factors, proteins, anti-inflammatory drugs, and antibiotics, which have been widely explored for anodized nano-engineered Ti, as described previously [277]. Table 4 presents a summary of key investigations on NiTi nanoengineering.

Currently, there is no research on the application of nanostructures on NiTi alloy surfaces on rotary endodontic files. A physical property of nanostructures of possible interest in irrigation is its wettability.

Wettability is usually measured as the contact angle from a sessile drop of water on the substrate surface. Shang et al. [278] found presence of NTs made the NiTi alloy surface reduced the contact angle making it more hydrophilic than untreated NiTi. This was again confirmed by Davoodian et al. [274] where the NTs and intertubular spaces allowed the liquid to penetrate and decrease the contact angle. Zhao et al. [268] found an increase in the contact angle after anodization into NP structures but a significant decrease in contact angle after hydrothermal treatment into NS structures.

Modifying NiTi instrument surfaces through nano-engineering has the potential to promote antimicrobial effects by fluid flow mechanics around NiTi files. It is envisaged that a file will function as both a shaping instrument as well as an activator of root canal irrigants. Conventionally, irrigation solutions facilitate disinfection of the canal space, removal of microorganisms and debris [279,280]. However, this only occurs after the canal has been sufficiently enlarged using endodontic files [281,282]. During instrumentation, the purpose of the irrigant is to lubricate the canal to reduce the friction between the file and dentin, improve cutting efficiency and keep the file cool in the tooth [280]. Currently, there is no literature that supports any rotary NiTi file system being able to simultaneously shape the canal and carry irrigant to the apical extent of the canal. There is limited penetration of irrigants using conventional syringe techniques [283,284], where clinicians are then reliant on adjunct activation techniques that require additional equipment, time and cost [285–289].

The Finishing-File, (F-file, PlasticEndo, LLC, Lincolnshire, IL, USA) is a single-use rotary finishing file that can be mounted on any existing rotary engine used for instrumentation. It is made of non-toxic plastic polymer embedded with fine abrasive diamonds [290], designed to remove dentinal wall debris and agitate the irrigating solution without further enlarging the canal shape. The rotary action and increase in surface area due to the diamond embedded surface of the F-file may have promoted improved surface wettability to induce laminar fluid flow [291]. Previous studies have demonstrated that the polymer finishing file creates greater fluid shear stress when in motion as the irrigant is displaced by the file forcing rapid fluid flow through a small gap between the file and the walls of the canal [290,291].

Increasing the wettability and surface area through nanostructures on NiTi rotary files may allow more irrigation fluid to be carried on the surface of the NiTi file into the apical portion of the canal. Currently, post-manufacture heat treatments result in an oxide layer that has no added functionality beyond imparting a distinct color hue to the surface of the file. In addition, contemporary instruments are designed with variations in taper over the active portion of the file to reduce the screw-in effect and risk of taper lock. In theory, the combination of nanostructures and variations in taper would allow for a very narrow gap between the file and canal walls for irrigation fluid to be displaced for irrigation exchange, simultaneously activating, and shaping the canal space.

5. Research gaps and future directions

Whilst nano-engineering shows promising potential for NiTi alloys there are some specific considerations in its clinical applications, particularly regarding its possible use on endodontic NiTi files. The following summarizes the research gaps and future perspectives relating to nanoscale surface modification of NiTi alloys:

- A novel design feature to functionalize the surface of NiTi endodontic files is suggested. Currently, post-manufacture heat treatments result in an oxide layer that imparts a distinct color to the surface of the file, however with no additional functionality to this layer. Using nanotechnology there may be a potential to utilize nanostructures for the added value of optimizing irrigation fluid dynamics within the root canal system. The feasibility of this as well as clinical applications need to be thoroughly investigated.
- Assessment of biocompatibility of nanostructured surface is still in its early stages. NTs have demonstrated to have good cytocompatibility and the amount of Ni leached is well tolerated [254]. Within the medical field, NiTi implanted devices have demonstrated excellent biocompatibility [22,297,298]. However, it remains unknown the potential for hypersensitivity reaction of nanoparticulates released from nano-engineered NiTi endodontic files.
- There is lack of investigations on the mechanical performance of NT or NP on NiTi endodontic files. It is unclear whether NT and NP will undergo microstructural and morphological changes when in contact with common endodontic irrigants such as NaOCl and EDTA. Also, the mechanical stability of nanostructures when used in shaping canals, particularly curved canals is unclear. Investigation on how well they perform in a clinical setting will need to be carried out.
- As more NiTi instruments are introduced into the market, with replica-like systems being commercialized worldwide, there is still very limited evaluation of their mechanical performance compared to the original file systems. This is also true with heat-treatments as there is very limited to no information available of newly developed proprietary heat treatment technologies. Currently there are inconsistencies in methods of mechanical testing of NiTi files and there is no standardization on the minimum quality of an instrument. More research is needed on understanding mechanical properties, type of metal alloy, geometric characteristics, cutting efficiency and shaping ability of newer NiTi systems so comparisons can be made between systems and manufacturers for continual improvement in the technology.
- Currently, we rely on various methods to carry disinfectants or medicaments into the canal, such as endodontic files, syringes, or rotary spiraling techniques. However, these techniques are inconsistent in their placement [299,300]. Success in functionalizing NiTi file surface through nanostructures may allow improved transportation of disinfectants and medicaments. This technology can potentially be further carried into drug loading on the surface or addition of growth factors on the surface of NiTi files as part of pulpal tissue regenerative procedures [301,302]. Finally, there may also be a potential in improving endodontic diagnosis by using NP or NT to assist in the detection of biological markers within the pulp space.

6. Conclusions

The super-elastic and shape-memory properties of NiTi has revolutionized the endodontic file industry. It is well known that surface and heat treatments have made NiTi files more resilient and flexible systems. However, most research have focused on NiTi's physical ability to shape the root canal space for adequate chemical disinfection to allow for subsequent obturation/sealing of the root canal space whilst still preserving sufficient tooth structure. A combination of mechanical and chemical disinfection protocols has been utilized to achieve adequate disinfection. More recently, there has been interest in surface functionalization of endodontic files such as added antimicrobial properties. With recent shifts and improvements in nano-engineering technology, there may be a possibility of customizing the surface of NiTi files for therapeutic or bioactive functions. This technology has yet to be fully established in NiTi endodontic files particularly in relation to its feasibility and mechanical stability. Outside of endodontics, such as in medical implant research, nanostructures have been well established to enhance bioactivity and drug delivery mechanisms. The future of NiTi

Table 4
Anodization of NiTi alloys to fabricate nanostructures.

Author, Year	NiTi Substrate	Anodization Conditions	Nanostructure	Characteristics/Applications
Kim et al. 2010 [253]	NiTi foils (56% Ni)	Voltage (20–80V); ethylene glycol containing electrolyte NH_4F content (0.25 wt%); electrolyte H_2O content (1.5 vol%); duration (5–10mins)	Nanotubes	First reported generation of NiTi nanotubes for use as an electrode material for pseudocapacitors.
Li et al. 2013, 2014 [256,257]	NiTi plates (50.8% Ni)	Voltage (20V–30V); non-aqueous ethylene glycol containing electrolyte NH_4F content (0.2M–0.4 M); electrolyte $(NH_4)_2SO_4$ content (0.15M–0.3 M); duration (90mins)	Nanotubes	Found Ni-doped TiO_2 nanotube arrays to have good performance with high sensitivity in detecting hydrogen atmospheres.
Hang et al. 2014 [258]	NiTi sheets (50.8% Ni)	Voltage (5–90V); electrolyte temperature (10–50 °C); ethylene glycol containing electrolyte NH_4F content (0.025–0.8 wt%); electrolyte H_2O content (0.0–1.0 vol%); duration (0.25–12 h)	Nanotubes	Measured variation in anodization parameters on the formation and structure of nanotubules. Changes in the parameters resulted in different diameters (15–70 nm) and lengths (45–1320 nm) of nanotubules.
Lee et al. 2014 [267]	NiTi foils (55.85–55.75% Ni)	Voltage (5–90V); ethylene glycol containing electrolyte NH_4F content (1.48g); electrolyte H_2O content (8.35 mL); duration (0.25–12 h)	Nanotubes	Demonstrated nanotubule coating can improve reendothelialization by increasing the cell spreading and migration of human aortic endothelial cells on NiTi. Potential to reduce restenosis rates.
Huan et al. 2014 [265]	NiTi sheets (50.6% Ni)	Voltage (20–50V); electrolyte temperature (room temperature); ethylene glycol containing electrolyte NH_4F content (0.5 wt%); electrolyte H_2O content (1.0 vol%); duration (10mins)	Nanotubes and micro-pitting	Formation of hybrid micro/nanostructures on biomedical NiTi alloys though a combination of electrochemical etching and anodization.
He et al. 2015 [260]	NiTi foil (50% Ni)	Voltage (60V); ethylene glycol containing electrolyte NH_4F content (0.25 wt%); electrolyte H_2O content (2.0 wt%); duration (6–12mins)	Nanotubes	Found nanotube arrays supported methanol oxidation for electrochemical applications and direct methanol fuel cells.
Hou et al. 2016 [259]	NiTi plates (50.8% Ni)	Voltage (30V); electrolyte temperature (30 °C); non-aqueous ethylene glycol containing electrolyte NH_4F content (0.2 M); electrolyte $(NH_4)_2SO_4$ content (0.15 M); duration (90mins)	Nanotubes	Demonstrated excellent catalytic activity and stability for direct methanol fuel cells.
Zhen et al. 2016 [292]	NiTi wire (50.8% Ni)	Voltage (40V); electrolyte temperature (5 °C); ethylene glycol containing electrolyte NH_4F content (0.25 wt%); electrolyte H_2O content (1.5 vol%); duration (5–15mins)	Nanotubes	Found nanotubules coated NiTi wire exhibited high extraction capability, good selectivity, and quick mass transference for Solid Phase Microextraction of UV filters for environmental water samples.
Lee et al. 2016 [269]	NiTi foils (55.75% Ni)	Voltage (85V); ethylene glycol containing electrolyte NH_4F content (1.48g); electrolyte H_2O content (8.35 mL); duration (4mins)	Nanotubes	Change in amount of ammonium fluoride in the electrolyte solution varies the diameters of the nanotubules. Found nanotubule coating reduced restenosis by reducing human aortic smooth muscle cell adhesion and proliferation while increasing human aortic endothelial cells migration, and collagen and elastin production.
Hang et al. 2017 [293]	NiTi rod (50.8% Ni)	Voltage (20–90V); ethylene glycol containing electrolyte NaCl content (0.3–0.9 M); electrolyte H_2O content (5–15 vol%); duration (1–10mins)	Nanopores	First use electrolyte composed of glycerol, H_2O and NaCl for the development of nanopores.
Hang et al. 2018 [294]	NiTi discs (50.8% Ni)	Voltage (10V); ethylene glycol containing electrolyte NaCl content (0.3 M); electrolyte H_2O content (5 vol%); duration (1–640mins)	Nanopores	Presence of nanopores improves the corrosion resistance of NiTi alloy. Overall good cytocompatibility and favorable antibacterial ability.
Shang et al. 2019 [278]	NiTi foils (58.72% Ni)	Voltage (30V); electrolyte temperature (20 °C); ethylene glycol containing electrolyte NH_4F content (2g); electrolyte H_2O content (10 mL); duration (30mins)	Nanotubes	Nanotubular surface is more hydrophilic compared to untreated surface. Found that the expression patterns of long noncoding RNAs in human coronary artery endothelial cells after nanotubular coatings changed.
Mohammadi et al. 2019 [295]	NiTi sheets (Nickel ingot 97% purity and titanium foil 96.82% purity preparations)	Voltage (25–80 V); ethylene glycol containing electrolyte NH_4F content (0.25 wt%); electrolyte H_2O content (1.5 vol%); duration (10–60mins)	Nanotubes	Enhanced corrosion resistance and reduced Ni release.
Mohammadi et al. 2019 [275]	NiTi sheets (Nickel ingot 97% purity and Ti foil 96.82% purity preparations)	Voltage (50 V); ethylene glycol containing electrolyte NH_4F content (0.25 wt%); electrolyte H_2O content (1.5 vol%); duration (10mins)	Nanotubes	Ability to control the rate of release of heparin. Potential for drug eluted stents.
Liu et al. 2019 [250]	NiTi sheets (50.8% Ni)	Voltage (30 V); ethylene glycol containing electrolyte NaCl content (0.6 M); electrolyte H_2O content (10 vol%); duration (10mins)	Nanopores, nanospindles	Anodically grown nanospores with amorphous structure on NiTi alloy can be converted to nanospindles after hydrothermal treatment in pure water at 200 °C.
Davoodian et al. 2020 [274]	NiTi discs (50% Ni)	Voltage (25 V); ethylene glycol containing electrolyte NH_4F content (0.2 wt%); electrolyte H_2O content (1.0 vol%); duration (60mins)	Nanotubes	Demonstrated the feasibility of loading nanotubes with vancomycin and coated with poly(lactic-co-glycolic acid) to control the rate of drug release within a therapeutic window to improve biocompatibility.
Liu et al. 2020 [296]	NiTi wires (50.8% Ni)	Voltage (15–25 V); ethylene glycol containing electrolyte NH_4F content (0.1–0.6 wt%); electrolyte H_2O content (1–2.5 vol%); duration (5–20mins)	Nanotubes, nanopores, nanoparticles	Variations in morphology of the nanostructures when modifying different parameters for use as fiber coatings for Solid Phase Microextraction
Zhao et al. 2021 [268]	NiTi rods (50.8% Ni)	Voltage (30V); electrolyte temperature (room temperature); glycerol containing electrolyte NaCl content (0.6 M); electrolyte H_2O content (10 vol%); duration (10mins)	Nanospindles	Fabricated nanospindles from nanopores. Nanospindles improves surface wettability and reduces Ni release. May promote re-endothelialization of NiTi stents.

alloy files include advanced nano-engineering that enable diagnosis and delivery of active therapeutics, however significant clinical translation challenges remain unaddressed.

Approvals

As this manuscript is a review paper, no ethics approvals are required. All reprint permissions for figures were obtained. There were no study subjects so no permission for participation were required.

CRediT authorship contribution statement

Wai-Sze Chan: Conceptualization, Investigation, Methodology, Formal analysis, Writing – original draft, Visualization. **Karan Gulati:** Validation, Methodology, Writing – review & editing, Supervision, Project administration. **Ove A. Peters:** Validation, Methodology, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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