

Current strategies in metallurgical advances of rotary niti instruments: a review

Abstract

Endodontic instruments made of NiTi shape-memory alloy have had a revolutionary impact on root canal treatment. This development has fostered a significant amount of research that is focused on enhancing metallic properties to improve clinical performance and safety which will significantly affect the outcome of root canal shaping and cleaning. The mechanical properties of nickel-titanium (NiTi) instruments are influenced by factors such as cross-section, flute design, raw material, and manufacturing processes. The integration of surface engineering (implantation or electropolishing) and/or microstructure control (heat treatment or innovative manufacturing techniques) into the endodontic file design has resulted in more favorable outcomes for instrument flexibility, fatigue resistance and cutting efficiency. This review will address the modifications in the metallurgy of the contemporary endodontic NiTi rotary instruments.

Keywords: nickel-titanium, plasma immersion ion implantation, cryogenic treatment, electropolishing, thermal nitridation, cyclic fatigue, heat treatment, m-wire; r-phase, controlled memory wire, austenite, martensite, phase transformation

Volume 9 Issue 1 - 2018

Swati Srivastava, Maymonah Abdurhman Alghadouni, Haneen Saleh Alotheem

Department of Conservative Dental Sciences, Qassim University, Saudi Arabia

Correspondence: Swati Srivastava, Assistant Professor, Department of Conservative Dental Sciences, College of Dentistry, Qassim University, Buraydah, Saudi Arabia, Email swatisrivastava412@gmail.com

Received: November 10, 2017 | **Published:** February 05, 2018

Abbreviations: NiTi, nickel titanium; PIII, plasma immersion ion implantation; PIRAC, powder immersion reaction assisted coating; EP, electropolishing; M, wire-martensitic wire, R phase, rhombohedral phase; CM, wire controlled memory wire, PTG, protaper gold; Hyflex EDM, hyflex electrical discharge machining

Introduction

NiTi alloy has been used as the raw material for making endodontic files. The interest in NiTi instrument research has not waned with time. In fact, there is a renewed interest in this field, notably through the application of modern research tools and techniques from other fields, making it a truly cross-disciplinary area of research. In 1988, Walia and colleagues introduced nickel-titanium (NiTi) files to endodontics.¹ Civjan et al.² first suggested the use of NiTi alloy for fabrication of hand and rotary instruments. Rotary NiTi instruments have become popular as they can clean and shape root canals with fewer procedural errors and more predictability than stainless steel hand files.³ However, these instruments are prone to separation without warning. Two modes of fractures have been identified for NiTi files: flexural fracture and torsional fracture. Flexural fracture occurs due to the cyclic fatigue experienced by the files within a curved canal. Repeated loading and unloading of NiTi files during instrumentation causes repetitive phase transformation resulting finally in torsional fracture of the instrument when it goes beyond the unrecoverable plastic deformation state.⁴ New materials and methods of manufacturing NiTi rotary instruments are in demand for better performance. The realization that the mechanical properties of near equiatomic NiTi alloys are strongly influenced by the stress-induced phase transformation taking place in this alloy and that the microstructural changes introduced by thermomechanical treatments can control this phase transformation constitutes the modern trend toward developing new rotary endodontic instruments with improved mechanical properties. This review will address the new developments in nickel-titanium metallurgy and their impact on rotary NiTi file systems.

Uniqueness of the nickel titanium alloys

A new endodontic file is composed of nickel and titanium atoms arranged in a body-centered cubic lattice structure called the *austenite* phase. When this file is placed in a curved canal, the atoms rearrange into a closely packed hexagonal array and the alloy is transformed into the more flexible *martensite* crystal structure. This molecular transition enables these files to bend easily and around severe curves without permanent deformation. When the stress is removed, the alloy reverts back to its initial austenite form. This stress-induced martensitic transformation is a unique property of NiTi alloys and makes this material one of the few alloys suitable for use in rotary endodontic instruments.⁵

Strategies in the alteration of NiTi alloy

In recent years, new forms of NiTi have been developed by modifying the alloy either by correcting the surface defects or variations in metal processing and file manufacturing.

Alteration in the surface of the alloy: Most fatigue failures nucleate from the surface, especially in the presence of high stress amplitude or surface defects.⁶ Attempts to enhance the surface of NiTi instruments, resistance to cyclic fatigue, and cutting efficiency have resulted in a variety of strategies which are discussed below.

Plasma immersion ion implantation: Plasma immersion ion implantation (PIII) was first introduced in the late 1980s by Conrad et al. and Tendys et al. During PIII, the specimen is placed in a chamber and immersed in the plasma; then a highly negative pulsating voltage is applied to the sample. Briefly, ion implantation is a line-of-sight process in which ions are extracted from plasma, accelerated, and bombarded into a device. Studies have shown successful results by implanting argon (Ar)- Lee et al.⁷ boron (B)- Wolle et al.⁸ nitrogen (N)- Rapisarda et al.⁹ Tripi et al.¹⁰ Gavini et al.¹¹ and plasma immersion Li et al.¹² Alves-Claro et al.¹³ without affecting the superelastic bulk mechanical properties of the alloy. Gavini et al.¹¹ showed that nitrogen

ion implantation improved the cyclic fatigue resistance of NiTi rotary instruments. Rapisarda et al.⁹ showed that ionic implantation demonstrated differences in surface characteristics, increased the cutting efficiency, and improved wear resistance.

Oxide formation on NiTi/titanium oxide coating: It is known that Ti has a higher affinity with oxygen, when compared to Ni. Therefore, with increased exposure time at moderate temperatures, the oxide formed is composed mainly of TiO₂ with a slow formation and growth. Aun DP et al.¹⁴ studied the influence of TiO₂ layer on the mechanical behavior of the endodontic instruments, as well as its corrosion resistance in NaOCl solution. They found an improvement in cutting efficiency and a high resistance to corrosion in NaOCl. The coated instruments showed a better performance in fatigue life after corrosion. They concluded that this characteristic should be maintained for the strained samples, since the TiO₂ layer can support relatively large deformations. Hence, a route to coat endodontic instruments with a flexible TiO₂ protective layer via dip-coating sol-gel technique has been shown to improve the cutting efficiency, corrosion behavior and fatigue resistance.

Thermal nitridation: The nitriding method known as powder immersion reaction assisted coating (PIRAC) produces TiN on NiTi. The modified surface consists of a thin outer layer of TiN and a thicker Ti₂Ni layer underneath.¹⁵ Nitriding at 300°C is not recommended as the SE character of the instrument may be lost. The instruments nitrided at 250°C are preferred for clinical application. The placement of a TiN layer on commercial rotary NiTi instruments significantly increases the corrosion resistance of files placed in contact with 5.25% NaOCl.

Cryogenic treatment: Deep dry cryogenic methods have been used to increase the wear, abrasion, corrosion resistance, microhardness and to improve the strength of metals. It has been seen to affect the entire cross section of the instrument rather than just the surface with no change in the elemental crystalline composition of the alloy.¹⁶ It involves suspending the metal over a super-cooled bath containing liquid N (-196a°C /-320°F) and then allowing the metal to slowly warm to room temperature. There are two mechanisms involved. First is more complete martensite transformation from the austenite phase following CT and second is the precipitation of finer carbide particles within the crystalline structure. Controversy exists about which mechanism to be the main one.^{17,18} According to Kim et al.¹⁹ cryogenically treated instruments had significantly higher microhardness. Vinothkumar et al.¹⁶ showed that CT significantly increased the cutting efficiency of NiTi instruments but it was not effective on the wear resistance. George et al.⁴ reported that CT significantly improved the cyclic fatigue resistance of NiTi rotary files.

Electropolishing / reverse plating: Electropolishing (EP) is a standard surface treatment process employed as a final finish during manufacturing of NiTi instruments. In this process, the surface chemistry and morphology are altered while surface imperfections are removed as dissolved metal ions. Typically, the instrument is immersed in a temperature- controlled bath of electrolyte and serves as the anode when it is connected to the positive terminal of a direct current power supply, and the negative terminal is attached to the cathode. As the current passes the surface of metal oxidizes and dissolves in the electrolyte. At the cathode, a reduction reaction occurs, which normally produces hydrogen. Electrolytes used most often are concentrated acid solutions with a high viscosity, such as

mixtures of sulfuric/phosphoric acid. Owing to a gain in total energy caused by the differences in the enthalpy of Ti and Ni oxides forming, the preferential oxidation of Ti on NiTi surface always occurs. Therefore, depending on the electrolytes and regimes employed, bare NiTi surfaces are built from Ti oxides with Ni concentrations from 2% to 7%.²⁰ In the process, the corrosion resistance of the metal is enhanced along with improved surface characteristics. Anderson et al.²¹ found that electropolished instruments performed significantly better in cyclic fatigue testing and, to a lesser extent, in static torsional loading. They concluded that the benefits of electropolishing are likely to be caused by a reduction in surface irregularities that serve as points for stress concentration and crack initiation. Cheung et al.²⁰ showed that the low cyclic fatigue life of NiTi instruments subjected to rotational bending was not enhanced by EP. They further reported that EP did not improve the resistance to corrosion of strain-cycled files. Most recently, Lopes et al.²² found that EP instruments demonstrated significant increases in cyclic fatigue resistance and exhibited fine surface cracks that assumed an irregular or zigzag path, whilst the non EP files had cracks running along the machining grooves. Thus, in reviewing all the studies it appears that EP enhance cyclic fatigue and peak torque values for NiTi instruments, the results of which may vary when the instruments are placed under significant flexion.

Alteration in the alloy microstructure by thermomechanical treatment

Thermal processing during the manufacturing of alloy

The mechanical behavior of NiTi alloy is determined by the relative proportions and characteristics of the microstructural phases. Heat treatment (thermal processing) is one of the most fundamental approaches toward adjusting the transition temperatures of NiTi alloys and affecting the fatigue resistance of NiTi endodontic files. De Vasconcelos et al.²³ found that the more martensitic NiTi alloy is the more flexible and the more fatigue resistant an instrument becomes that produces a better arrangement of the crystal structure and changes in the relative percentage of phases present in the alloy. Enhancements in these areas of material management have led to the development of the next-generation endodontic instruments which are discussed below.

M-wire

NiTi can have 3 different forms: martensite, stress-induced martensite (SE), and austenite. When the material is in its martensite form, it is soft and ductile and can easily be deformed. SE NiTi is highly elastic, whereas austenitic NiTi is quite strong and hard. The equiatomic NiTi alloy has all these properties, with the specific expression being dependent on the temperature at which it is used. A series of proprietary thermomechanical processing procedures has been developed with the objective of producing SE NiTi wire blanks that contain the substantially stable martensite phase under clinical conditions. The martensitic phase transformation has excellent damping characteristics because of the energy absorption characteristics of its twinned phase structure. In addition, the martensitic form of NiTi has an excellent fatigue resistance.^{24–27} M-wire (Dentsply Tulsa-Dental Specialties, Tulsa, OK, USA) was introduced in 2007 that contains portions that are in both the deformed and microtwinned martensitic, premartensitic R-phase, and are austenite whilst maintaining a pseudoelastic state.^{28,29} The austenite-finish temperature (Af) of M-Wire is around (45°C–50°C)

as shown by TMDSC analysis by Alapati et al.³⁰ The temperature range for phase transformation, suggests that these instruments made from M-Wire would be essentially in the martensitic phase at room temperature. M-Wire instruments include Dentsply's ProFile GT Series X, ProFile Vortex, ProTaper Next files, Path Files, WaveOne and Reciproc (VDW, Munich, Germany). ProFile GTX was launched in 2008. The manufacturer claimed that it has greater flexibility and an increased resistance to cyclic fatigue when compared to traditional NiTi alloys³¹ WaveOne (2011) exhibited improved resistance to cyclic fatigue and good torsional properties compared with conventional wire based instruments. Johnson et al.²⁹ reported that instruments made from M-Wire with a ProFile design exhibited nearly 400% more resistance to cyclic fatigue than SE wire instruments of the same size. Gao et al.³² compared the cyclic fatigue resistance of instrument made from M-Wire and regular SE wire at two different rotational speeds. More than 50% of broken files made of SE wire exhibited multiple crack-initiation sites compared with the single crack initiation on files made of M-Wire.

R phase

Heat treatment of conventional NiTi wires that are in the austenite phase transforms them into a rhombohedral crystal structure called as an intermediate R-phase between austenite and martensite.³³ It can be temperature-induced and stress-induced. The R-phase shows good superelasticity and shape memory effects; its Young's modulus is typically lower than that of austenite. Thus, an instrument made out of R-phase wire would be more flexible.³⁴ Once the R-phase is identified, wire in this state can be twisted. The twisting optimizes the grain structure in the metal, as grinding is claimed to weaken the metal's structure at the molecular level and create microfractures on its surface, both of which can lead to file fracture.³⁵ In 2008, SybronEndo (Orange, CA, USA) developed files by twisting the intermediate alloy, then further heat-treating to produce Twisted Files (TF) and K3XF. R-phase possesses lower shear modulus than martensite and austenite, and the transformation strain for is less than one-tenth that of martensitic transformation. At ambient and body temperatures, R phase instrument is fully austenite. The Af temperature of TF is ranging between (17.62-18.88°C).³⁴ Moreover, TF present a 2-step transformation giving flexibility to files through an apparent R-phase.³⁶ Recent reports have stated R-phase provides greater flexibility and increased resistance to flexural fatigue.³⁴⁻³⁸ However, Park et al.³⁹ found that this manufacturing method fails to provide any beneficial effect with regard to torsional fracture.

Controlled memory NiTi alloys (CM Wire) (2010)

CM Wire (DS Dental, Johnson City, TN) is a novel NiTi alloy with flexible properties that was introduced in 2010. It is manufactured by a proprietary thermo-mechanical process aimed to increase the flexibility, reduce the shape memory, raise the transformation temperatures (Af to about 50°C) and obtain stable martensite at the body temperature. This allows the instruments to be pre-curved prior to placing them into the root canal. Sterilization of the files will return them to their original shape. CM NiTi file systems available include Hyflex CM (Coltene Whaledent, USA), Typhoon CM (Clinician's Choice Dental Products, USA) and ProFile Vortex Blue (Dentsply). The Af temperature for most conventional SE NiTi files is at or below room temperature, whereas the Af of CM files is clearly above body temperature. As a result, the conventional NiTi files are in the

austenite phase during clinical use, whereas CM files in addition to the austenite, also contain martensite and R-phase. It was found that the Af temperature of Hyflex CM and Typhoon CM was about 47°C, and 55°C respectively suggesting that this instrument at body temperature will be in a mixed martensitic R-phase and austenitic structure.^{23,40} Shen Y et al.²⁵ found that CM instruments were nearly 300% to 800% more resistant to fatigue failure than instruments made from conventional NiTi wire. The square configuration of NiTi instruments made from CM Wire showed a significantly longer fatigue life than the triangular configuration. Therefore, the design of the instrument should also be taken into account because it is an important determinant of the fatigue lifetime.

Thermal processing after machining of files / post machining heat treatment

Recently, a new heating process after the machining of the files has been used to overcome machining process defects, and to modify the crystalline phase structure. It has been reported that after thermal cycling, the martensitic transformation of NiTi alloys occurs in 2 stages instead of one. The 1-stage transformation (A-M) happens in Ni-rich NiTi alloys, whilst 2-stage transformation (A-R-M) happens after additional heat treatment. The heat treatment forms finely dispersed Ti₃Ni₄ precipitates in the austenitic matrix. Consequently, the R-phase is formed in preference to martensite due to the presence of Ti₃Ni₄ fine particles. However, the alloy needs additional cooling to form martensite and hence, martensitic transformation occurs in 2 steps (A-R-M).³³

Vortex blue

It is a newly developed NiTi rotary instrument made from M-Wire with improved fatigue resistance, cutting efficiency, flexibility, and canal centering capability.⁴¹ Its Af temperatures is around 38°C. Studies have shown that vortex blue had a 2-stage transformation. This can be understood by considering that R-phase is another potential martensite candidate that possesses a lower shear modulus and a shorter transformation strain.⁴² Vortex Blue instruments show a unique "blue color" compared with traditional SE NiTi instruments. The "blue-color" oxide surface layer of Vortex Blue files is a result of the proprietary manufacturing process. The relatively hard titanium oxide surface layer on the Vortex Blue instrument may compensate for the loss of hardness compared with ProFile Vortex M-Wire while improving the cutting efficiency and wear resistance. Recently, Gao et al.²⁴ evaluated the impact of raw materials (including stainless steel, conventional SE NiTi, M-Wire NiTi, and Vortex Blue NiTi) on the fatigue resistance of rotary instruments by rotating the files in an artificially constructed stainless steel canal. Vortex Blue was ranked first in both fatigue life and flexibility followed by M-Wire, SE wire, and finally stainless steel.

Protaper gold (PTG)

They have the same geometries as ProTaper Universal with a convex triangular cross section and progressive taper. Post heat treatment is applied after the flutes of a file have been manufactured. The temperature used is in a range of 370-510°C for a variable period of time. Files exhibit two stage specific transformation behavior and high Af temperature around 50°C similar to CM wire.⁴³ These findings explain the higher resistance of PTG instruments to cyclic fatigue than PTU. PTG has considerably less shape memory than NiTi. So,

clinicians should be not surprised to find an unopened package of files which exhibit a slight degree of curvature. This is not a defect, but rather, an advantage as supposed by the manufacturer. Further, upon removing a PTG file from a curved canal, the file will be noted to follow the anatomy of root canal being shaped.

Waveone gold

WaveOne Gold is the result of a unique heat-treatment prior and after file manufacturing. The SE NiTi alloy is subjected to special heat treatment under constant strain in a range of 3-15 kg in a temperature range of about 410° to 440°C. After machining the working portion of the file, the finished instrument is heat treated a second time in a range of 120°C to 260°C. The Af temperature is between 40°C -60°C. The manufacturer claims that the gold technology improves the flexibility and strength of the instrument. The off-centred parallelogram-shaped cross-section design of WaveOne Gold could enhance its torsional resistance.

Hyflex EDM

Hyflex EDM (Coltene Whaledent, Cuyahoga Falls, OH) is manufactured using the technique of electrical discharge machining (EDM). EDM is a noncontact thermal erosion process used to machine electrically conductive materials using controlled electrical discharges. The electrical sparks cause a local melting and partially evaporation of small portions of material that are removed from this local area leaving a typical crater-like surface finish. After cutting and cleaning is accomplished through ultrasonics in an acid bath, the instrument is heat treated at temperature ranging between 300-600°C for 10 min to 5 hours before or after the cleaning process. EDM files have Af temperatures over 52°C.⁴⁴ Additionally, the EDM process produces a non-directional surface finish, thereby avoiding inducement of early material failure that results from conventional grinding techniques. According to the manufacturer HyFlex may be up to 300% more fatigue-resistant, compared with other rotary NiTi instruments. They also state that sterilization will result in the instrument regaining its shape. Peters et al.²⁷ found that more than half of instruments that underwent plastic deformation, recovered their original shape during a sterilization cycle. However, the small instruments were often permanently deformed. Therefore, caution should be exercised regarding reuse of small HyFlex rotary instruments. Dentists may need to apply less apical pressure against canal walls than with conventional SE NiTi files of the same size and taper.

K3 XF

K3XF was developed by SybronEndo in 2011 which takes advantage of R-phase technology. However, it is fabricated by a grinding process rather than a twisting process. A special heat treatment is performed on K3XF files after the grinding process, which not only enhances the flexibility and strength, but also modifies the crystalline structure of the alloy to accommodate some of the internal stress caused by the grinding process.⁴⁵ K3 and K3XF instruments are identical in shape and differ only in that K3XF instruments undergo post-machining heat treatment.³⁵ K3XF instruments have an Af temperature below 37°C. Therefore, it has an austenite structure at body temperature and would exhibit a super elastic property during clinical application. The heat treatment processing used for K3XF,

may modify the transformation temperature by releasing crystal lattice defects and diminishing internal strain energy. Numerous micropores with various diameters can be seen on the surface of the instrument flute on K3XF instruments. These small pores do not contribute to the failure, but serve as a local stress/strain discontinuity from which the crack nucleates.⁴⁶

XP endo shaper

XP endo shaper (FKG Dentaire, La-Chaux-de-Fonds, Switzerland) was introduced in 2016 with 0.30 diameter and 0.1 taper that could expand to 0.4 taper. This file has a retracted form to rectilinear geometry when it is in a martensitic phase (rest position or static) and a structured form when in the austenite phase (working position or dynamic state). The transition from the martensite phase to the austenite phase occurs naturally in the body temperature between 32°C and 37°C with Af temperature around 35°C. In dynamic state, the instrument has a twisted shape, with several twists twisted along its length.

Effect of autoclaving on the new forms of NiTi Files

Since heat-treatment affects the physical properties of NiTi alloys, autoclaving could modify their physical properties of M wire, R phase and CM alloys. However, up to seven sterilization cycles have not significantly impacted the flexibility or fracture resistance of M-wire (ProFile Vortex), R-phase (TF) or CM-wire NiTi instruments.⁴⁷

Conclusion

Recent advancements in the manufacturing process of NiTi alloys have allowed for the development of rotary endodontic file systems that are more flexible, less likely to fracture and more capable of maintaining the original canal position than their predecessors. New NiTi endodontic files with superior properties have been developed through special thermomechanical processing, which gives them better flexural fatigue resistance than files made from conventional NiTi alloy. Although the detailed thermomechanical process is unknown due to the protection of intellectual property, we can evaluate the influence of the thermomechanical treatments on the mechanical properties indirectly by analyzing the phase transformation behavior of the alloy. Based on present data, the advances in material processing appear to offer substantial benefits to the efficacy, efficiency, durability and safety of contemporary endodontic instruments. However, technological developments in metallurgy offer the possibility of further enhancement of these materials, with one of the most promising processes being post-machining heat treatment.

Funding

None.

Acknowledgements

None.

Conflicts of interest

None.

References

1. Walia HM, WA, Gerstein H. An initial investigation of the bending and torsional properties of Nitinol root canal files. *Journal of endodontics*. 1988;14(7):346–351.
2. Civjan S, Huget EF, DeSimon LB. Potential applications of certain nickel–titanium (nitinol) alloys. *J Dent Res*. 1975;54(1): 89–96.
3. Short JA, Morgan LA, Baumgartner JC. A comparison of canal centering ability of four instrumentation techniques. *Journal of endodontics*. 1997; 23(8):503–507.
4. George GK, Sanjeev K, Sekar M. An *in vitro* evaluation of the effect of deep dry cryotreatment on the cutting efficiency of three rotary nickel titanium instruments. *J Conserv Dent*. 2011;14(2):169–172.
5. Thompson SA. An overview of nickel–titanium alloys used in dentistry. *Int Endod J*. 200;33(4):297–310.
6. Bahia MG, Buono VT. Decrease in the fatigue resistance of nickel–titanium rotary instruments after clinical use in curved root canals. *Oral surgery, oral medicine, oral pathology, oral radiology, and endodontics*. 2005;100(2):249–255.
7. Lee DH, Park B, Saxena A, et al. Enhanced surface hardness by boron implantation in Nitinol alloy. *Journal of endodontics*. 1996;22(10):543–546.
8. Wolle CF, Vasconcellos MA, Hinrichs R, et al. The effect of argon and nitrogen ion implantation on nickel–titanium rotary instruments. *Journal of endodontics*. 2009;35(11):1558–1562.
9. Rapisarda E, Bonaccorso A, Tripi TR, et al. The effect of surface treatments of nickel–titanium files on wear and cutting efficiency. *Oral surgery, oral medicine, oral pathology, oral radiology, and endodontics*. 2000;89(3):363–368.
10. Tripi TR, Bonaccorso A, Rapisarda E, et al. Depositions of nitrogen on NiTi instruments. *Journal of endodontics*. 2002;28(7):497–500.
11. Gavini G, Pessoa OF, Barletta FB, et al. Cyclic fatigue resistance of rotary nickel–titanium instruments submitted to nitrogen ion implantation. *Journal of endodontics*. 2010;36(7):1183–1186.
12. Li UM, Iijima M, Endo K, et al. Application of plasma immersion ion implantation for surface modification of nickel–titanium rotary instruments. *Dental materials journal*. 2007;26(4):467–473.
13. Alves–Claro AP, Claro FA, Uzumaki ET. Wear resistance of nickel–titanium endodontic files after surface treatment. *Journal of materials science Materials in medicine*. 2008;9(10):3273–3277.
14. Aun DP, Peixoto IF, Houmard M, et al. Enhancement of NiTi superelastic endodontic instruments by TiO₂ coating. *Materials science & engineering C, Materials for biological applications*. 2016;68:675–680.
15. Starosvetsky D, Gotman I. Corrosion behavior of titanium nitride coated Ni–Ti shape memory surgical alloy. *Biomaterials*. 2000; 22(13):1853–1859.
16. Vinothkumar TS, Miglani R, Lakshminarayanan L. Influence of deep dry cryogenic treatment on cutting efficiency and wear resistance of nickel–titanium rotary endodontic instruments. *Journal of endodontics*. 2007;33(11):1355–1358.
17. Barron RF. Cryogenic treatment of metals to improve wear resistance. *Cryogenics*. 1982;22(8):409–413.
18. Huang JY, Zhu YT, Liao XZ, et al. Microstructure of cryogenic treated M2 tool steel. *Materials Science and Engineering: A*. 2003; 339(1):241–244.
19. Kim JW, Griggs JA, Regan JD, et al. Effect of cryogenic treatment on nickel–titanium endodontic instruments. *Int Endod J*. 2005;38(6):364–371.
20. Cheung GS, Shen Y, Darvell BW. Does electropolishing improve the low–cycle fatigue behavior of a nickel–titanium rotary instrument in hypochlorite? *Journal of endodontics*. 2007;33(10):1217–1221.
21. Anderson ME, Price JW, Parashos P. Fracture resistance of electropolished rotary nickel–titanium endodontic instruments. *Journal of endodontics*. 2007;33(10):1212–1216.
22. Lopes HP, Elias CN, Vieira VT, et al. Effects of electropolishing surface treatment on the cyclic fatigue resistance of BioRace nickel–titanium rotary instruments. *J Endod*. 2010;36(10):1653–1657.
23. De Vasconcelos RA, Murphy S, Carvalho CA, et al. Evidence for Reduced Fatigue Resistance of Contemporary Rotary Instruments Exposed to Body Temperature. *Journal of endodontics*. 2016;42(5):782–787.
24. Gao Y, Gutmann JL, Wilkinson K, et al. Evaluation of the impact of raw materials on the fatigue and mechanical properties of ProFile Vortex rotary instruments. *Journal of endodontics*. 2012;38(3):398–401.
25. Shen Y, Qian W, Abtin H, et al. Fatigue testing of controlled memory wire nickel–titanium rotary instruments. *J Endod*. 2011;37(7): 997–1001.
26. Shen Y, Qian W, Abtin H, et al. Effect of environment on fatigue failure of controlled memory wire nickel–titanium rotary instruments. *Journal of endodontics*. 2012;38(3):376–380.
27. Peters OA, Gluskin AK, Weiss RA, et al. An *in vitro* assessment of the physical properties of novel Hyflex nickel–titanium rotary instruments. *Int Endod J*. 2012;45(11):1027–1034.
28. Alapati SB, Brantley WA, Iijima M, et al. Metallurgical characterization of a new nickel–titanium wire for rotary endodontic instruments. *J Endod*. 2009;35(11):1589–1593.
29. Johnson E, Lloyd A, Kuttler S, et al. Comparison between a novel nickel–titanium alloy and 508 nitinol on the cyclic fatigue life of ProFile 25/.04 rotary instruments. *J Endod*. 2008;34(11):1406–1409.
30. Alapati SB, Brantley WA, Iijima M, et al. Micro–XRD and temperature–modulated DSC investigation of nickel–titanium rotary endodontic instruments. *Dent Mater*. 2009;25(10):1221–1229.
31. Al–Hadlaq SM, Aljarbou FA, AlThumairy RI. Evaluation of cyclic flexural fatigue of M–wire nickel–titanium rotary instruments. *Journal of endodontics*. 2010;36(2):305–307.
32. Gao Y, Shotton V, Wilkinson K, et al. Effects of raw material and rotational speed on the cyclic fatigue of ProFile Vortex rotary instruments. *J Endod*. 2010;36(7):1205–1209.
33. Otsuka K, Ren X. Physical metallurgy of Ti–Ni–based shape memory alloys. *Progress in Materials Science*. 2005;50(5):511–678.
34. Hou X, Yahata Y, Hayashi Y, et al. Phase transformation behaviour and bending property of twisted nickel–titanium endodontic instruments. *Int Endod J*. 2011;44(3): 253–258.
35. Gutmann JL, Gao Y. Alteration in the inherent metallic and surface properties of nickel–titanium root canal instruments to enhance performance, durability and safety: a focused review. *Int Endod J*. 2012;45(2):113–128.
36. Shen Y, Zhou HM, Zheng YF, et al. Metallurgical characterization of controlled memory wire nickel–titanium rotary instruments. *J Endod*. 2011;37(11):1566–1571.
37. Gambarini G, Gerosa R, De Luca M, et al. Mechanical properties of a new and improved nickel–titanium alloy for endodontic use: an evaluation of file flexibility. *Oral surgery, oral medicine, oral pathology, oral radiology, and endodontics*. 2008;105(6):798–800.
38. Da Cunha Peixoto IF, Pereira ES, da Silva JG, et al. Flexural fatigue and torsional resistance of ProFile GT and ProFile GT series X instruments. *J Endod*. 2016;36(4):741–744.

39. Park SY, Cheung GS, Yum J, et al. Dynamic torsional resistance of nickel–titanium rotary instruments. *Journal of endodontics*. 2010;36(7):1200–1204.
40. Shen Y, Coil JM, Zhou H, et al. HyFlex nickel–titanium rotary instruments after clinical use: metallurgical properties. *Int Endod J*. 2013;46(8):720–729.
41. Shen Y, Zhou HM, Zheng YF, et al. Current challenges and concepts of the thermomechanical treatment of nickel–titanium instruments. *J Endod*. 2013;39(2):163–172.
42. Shen Y, Zhou H, Coil JM, et al. ProFile Vortex and Vortex Blue Nickel–Titanium Rotary Instruments after Clinical Use. *Journal of endodontics*. 2015;41(6): 937–942.
43. Hieawy A, Haapasalo M, Zhou H, et al. Phase Transformation Behavior and Resistance to Bending and Cyclic Fatigue of ProTaper Gold and ProTaper Universal Instruments. *J Endod*. 2015;41(7):1134–1138.
44. Iacono F, Pirani C, Generali L, et al. Structural analysis of HyFlex EDM instruments. *Int Endod J*. 2017;50(3):303–313.
45. Gambarini G, Plotino G, Grande NM, et al. Mechanical properties of nickel–titanium rotary instruments produced with a new manufacturing technique. *Int Endod J*. 2011;44(4):337–341.
46. Haapasalo M, Shen Y. Evolution of nickel–titanium instruments: from past to future. *Endodontic Topics*. 2013; 29(1):3–17.
47. Casper RB, Roberts HW, Roberts MD, et al. Comparison of autoclaving effects on torsional deformation and fracture resistance of three innovative endodontic file systems. *J Endod*. 2011;37(11):1572–1575.