Acta Scientific MEDICAL SCIENCES (ISSN: 2582-0931)

Volume 8 Issue 12 December 2024

Review Article

Nickel-titanium Alloy in Endodontics – Evolution and Perspectives

Oana Amza[1#], Georgiana Gheorghe[1#], Laura Iosif[2*], Ana-Maria Țâncu[2*] and Bogdan Dimitriu[1]

[1]*Department of Endodontics, Faculty of Dental Medicine, "Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania*

[2]*Department of Prosthetic Dentistry, Faculty of Dental Medicine, "Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania*

***Corresponding Author:** Laura Iosif: laura.iosif@umfcd.ro Department of Prosthetic Dentistry, Faculty of Dental Medicine, "Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania and Ana-Maria Țâncu: ana-maria.tancu@umfcd.ro Department of Prosthetic Dentistry, Faculty of Dental Medicine, "Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania.

#This author equally contributed to the first author.

DOI: 10.31080/ASMS.2024.08.1973

Received: November 11, 2024

Published: November 21, 2024

Abstract

The nickel-titanium alloy (NiTi) has been the subject of much research in endodontics. Research advances have focused mainly on the design, shape and geometry of NiTi files, as well as metallurgy and mechanical properties. Due to their importance for the NiTi instruments, these have been extensively investigated, considering all the details underlying the clinical behavior of current endodontic instruments. The association of crystallographic structure, heat treatment, surface treatment techniques, machining methods, design and kinematics of the instruments during shaping the root canal decisively influences their clinical behavior.

Keywords: Nickel-Titanium (NiTi) Alloy; Crystallographic Phases; Rotary Endodontics

Introduction

The introduction of the nickel-titanium alloy in endodontics marked a real milestone in its history. Shaping root canals was decisively influenced by the development of rotary instruments based on NiTi alloy, which allowed easier, safer, more efficient and predictable approach, shorter preparation time and less operator fatigue.

In addition to design and technique, endodontic instrumentation is greatly influenced by the alloy used in the manufacturing process of the rotary files.

The widespread use of NiTi rotary instruments, which have almost completely replaced stainless steel ones, is essentially a result of the two most important features of the NiTi alloy: superelasticity and shape memory effect.

The evolution of rotary instrumentation has been permanently influenced by the improvement of the metallurgical characteristics of the nickel-titanium alloy, meant to increase resistance, flexibility, cutting efficacy and safety of the instrument.

The importance of these developments will be presented further.

In 1959 the metallurgist scientist William J. Buehler, was working at Naval Ordinance Laboratories, in Maryland, the United States, aiming to develop a heat and corrosive resistant alloy. He created a binary alloy made of 55% nickel and 45% titanium, which he named Nitinol, representing its elemental components and place of origin: the “Ni” and “Ti” are the atomic symbols for nickel and titanium and the “NOL” stands for Naval Ordinance Laboratory. The shape memory aspect of nitinol was not discovered until 1961.

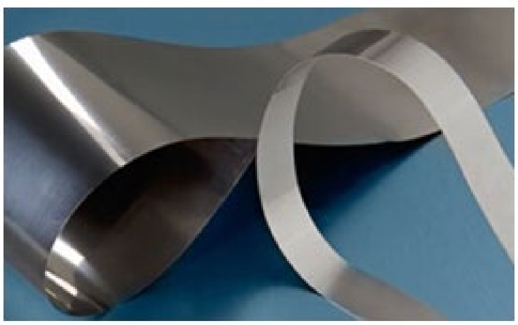

Figure 1: Nitinol Foil - Stanford Materials [1].

This was not the first shape memory alloy discovered. A gold-cadmium alloy was developed in 1939, but the shape memory effect was minimal, and the material was extremely expensive.

Today nickel titanium alloys have various applications in biomedical devices, automotive actuators, micro-electromechanical systems (MEMSs), damping systems in structural engineering, physical vapor deposition processes suitable for thin film coatings, and aero-space industries.

One of the first medical applications of Nitinol were vascular stents, followed by surgical implants - as total hip arthroplasty - and eyeglasses frames [2]. The alloy provides a possibility to make self-locking, self-expanding and self-compressing implants.

The first generation of NiTi alloys used in dentistry was introduced in 1971 [3] to produce orthodontic wires marketed by the Unitek Corporation - now known as 3M Unitek.

In 1975 the concept of fabrication of endodontic instruments using NiTi was proposed [4], but the first manual NiTi endodontic instruments were introduced by Walia, Brantley and Gerstein in 1988 [5].

Currently, the nickel titanium alloy used in endodontics has an equiatomic composition with a 1:1 stoichiometric ratio between nickel (56%) and titanium (44%).

During the last three decades NiTi endodontic instruments have undergone numerous changes through design modifications, surface treatments, and heat treatments to improve root canal preparation outcomes and reduce the risks associated with instrumentation during endodontic treatment, especially the most important problem of NiTi files - intracanal fracture.

Heat treatment is one of the most important approaches to increase the fatigue resistance and flexibility of nickel titanium endodontic instruments.

NiTi is an intermetallic compound with the intrinsic ability to modify its atomic bonding.

As with other metallic alloys, the NiTi alloy can exist in several crystallographic arrangements. The changes in the alloy arrangement may result from stress application or temperature effects [6].

Due to changes in temperature and mechanical pressure, nitinol has two distinct phases of the crystalline structure, namely the austenitic phase and the martensitic phase. Austenite is the crystal phase shown by alloy at high temperature. When the temperature decreases, austenite gradually converts to martensite (Figure 2).

The process of changing (shifting) from the austenitic phase to the martensitic phase can take place by temperature, mechanical stress or simultaneous action of both components. The shifting from austenite to martensite can occur at the same temperature or at shifting temperatures [7].

The austenitic phase is a stable high-temperature phase, with a body centered cubic lattice, an elastic modulus of 80-90 GPa, superelastic properties and low plastic deformation.

Martensitic phase is a hexagonal lattice, only stable in a lower temperature range, with an elastic modulus of 30-40 GPa, shape memory properties, great flexibility and easily deformable due to its high plasticity.

Intermediate R phase is a hybrid rhombohedral distorted phase, which is formed when transition occurs from austenite to martensitic phase, with an elastic modulus smaller than the martensitic phase.

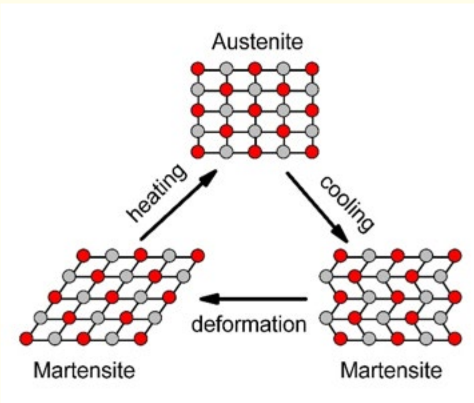

Figure 2: The phases of nickel titanium alloy structure transformation [8].

In the process of martensite and austenite transformation, there are four kinds of temperatures [9]:

- A_s: The temperature at which martensite begins to convert to austenite during the process of temperature rise.
- A_f: The temperature at which martensite finishes the conversion into austenite during the process of temperature rise.
- M_s: The temperature at which austenite begins to convert to martensite during the process of temperature drop.
- M_f: The temperature at which austenite finishes the conversion into martensite during the process of temperature drop.

The phase transformation of nitinol has a thermal hysteresis, so A_s is not equal to M_f, and, for the same reason, A_f is not equal to M_s (Figure 3).

The martensitic phase is also called the cold phase because it occurs at lower temperatures, whereas the austenitic phase is called the hot phase because it forms and stabilizes at higher temperatures [11]. The composition of the alloy directly influences the temperature values at which these two phases are formed and stabilized.

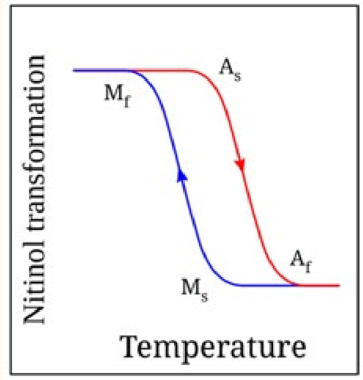

Figure 3: Nitinol transformation hysteresis diagram [10].

The most important properties of nickel titanium alloy are on the one hand corrosion resistance and biocompatibility, due to its excellent stability and on the other hand resistance to fatigue, bending, and torsion, due to a higher flexibility limit [7].

Both superelasticity and shape memory effect are defining characteristics of the NiTi alloy used for endodontic purposes.

Superelasticity is the ability to undergo great deformations, on the order of 5-10%, and to be able to recover them completely during the unloading phase without highlighting plastic phenomena. Shape memory effect is the aptitude to "remember" a certain initial geometric shape and the ability of deformed NiTi to recover its original shape when heated, due to phase transformation of stable deformed martensite to stable austenite phase [11,12].

If the temperature is above austenite finish temperature (A_f), the alloy is in the austenitic state - stiff, hard, with superior superelastic properties. If the temperature is below martensite finish temperature (M_f), the nickel titanium alloy is in the martensitic state - soft, ductile, can easily be deformed, with shape memory effect [11].

A change in the transformation temperatures - M_s, M_f, A_s, A_f - of the NiTi alloy, achievable by thermal and mechanical treatment or variation in the chemical composition, is the most important possibility for manufacturers to alter the phase composition and consequently the mechanical properties of the NiTi alloy used for endodontic instruments [12].

The manufacturing process of NiTi endodontic instruments is a complex one, consisting of three successive processes, including vacuum melting/casting, press forging and rotary swaging, and rod/wire rolling. These are followed by wiredrawing, annealing and descaling, fine-wire and profile drawing, cleaning and conditioning, and machining and milling [7].

Along the almost three and a half decades since the first NiTi instruments have been used for endodontic instrumentation, the alloy has undergone continuous changes to improve clinical performance, effectiveness and reliability, enhance shaping ability in complex endodontic systems, increase safety of use and decrease the duration of endodontic treatment.

These objectives targeted essential elements, represented by both microscopic elements concerning the alloy's intrinsic structure and macroscopic features aiming the kind of manufacturing process of the instrument and its design features, and the type of rotation movement.

All these developments are reflected in the successive evolution of several generations of rotary instruments, each with specific physical-chemical characteristics and clinical behavior:

- First generation - rounded noncutting tip, radial land, fixed taper, negative rake angle.
- Second generation - based on design, multiple tapers, positive rake angle.
- Third generation - based on advanced nickel titanium alloys, thermomechanical treatment, development of M wire, R phase, CM wire, blue and gold surface conditioning.
- Fourth generation - based on different kinematics, introducing reciprocating motion, single file system and single use concept, adaptive motion.
- Fifth generation - based on changes of instrument design, eccentric center of rotation, better debris extrusion due to reduced taper lock and noncontact space, swaggering effect.
- Sixth generation - engine driven instruments for glide path, innovation in irrigation (SAF, XP finisher), specific retreatment files.
- Seventh generation - based on new manufacturing processes, twisted files, shape settings (TRUshape, XP shaper), electric discharge machining (EDM) [13].

These continuous transformations refer to 4 categories of characteristics specific to endodontic instruments made of NiTi alloy: structural design, manufacturing treatment, metallurgical development and type of movement [13].

The crystallographic structuring of the NiTi alloy is directly influenced by heat treatment which determines important changes regarding the specific phases. It is a well-established fact that the mechanical properties, transformation temperatures and phase compositions of NiTi endodontic alloy are decisively influenced by the proprietary thermomechanical treatment [12].

The metallurgical tests performed for the evaluation of NiTi rotary instruments include the following:

- **Differential Scanning Calorimetry (DSC):** It is the most used metallurgical test in endodontics, first introduced in 2002 [14]. It evaluates the structure of the NiTi alloys using precise measurements of the difference in thermal power supplied to a test specimen and an inert control specimen heated at the same rate. This test was also used to investigate the modification of the NiTi alloy after clinical use [15].
- **Energy-Dispersive X-ray Spectroscopy (EDS):** This test allows the determination of nearequiatomic composition of NiTi instruments, and the detection of any other materials present as inclusions in the alloy or as adherent deposits on the surface [15,16].
- **Atomic Force Microscopy:** It is used for qualitative and quantitative information on the NiTi instrument's topography, evaluating the surfaces irregularities of the endodontic instruments and their changes after clinical use, multiple autoclave cycles and immersion in irrigating solutions [15].
- **X-ray diffraction (XRD):** It allows the determination of the crystallographic phase organization of the NiTi alloy and to investigate the impact of thermal treatments on phase configuration in instruments.

- **Metallographic Analysis:** It uses scanning electron microscopy to identify the grains of austenite and martensite in the NiTi alloy, to complete the results of XRD and EDS.
- Micro-Raman Spectroscopy and Focused Ion Beam Analysis are methods used to investigate the surface of NiTi instruments to assess the presence of surface layers or coatings [17].
- **Auger Electron Spectroscopy:** It evaluates the chemical composition of the alloy in the surface layers, up to a depth of a few micrometers [18].

The metallurgical developments of NiTi alloy successively included:

Conventional NiTi alloy

It consisted of austenite phase, with superelastic properties. The endodontic files have been manufactured by grinding processes. Examples of rotary systems: Quantec, ProFile, Light speed, Greater Taper.

Figure 4: Quantec rotary system [19].

M-wire

It was developed by Tulsa Dental in 2007, after a complex heat treatment and a special stretching treatment of a conventional austenitic NiTi alloy. The result consists of an alloy comprising a large amount of stable martensite at room temperature, with a reduced stiffness and increased elasticity [13]. Such instruments exhibit improved flexibility, fatigue resistance, and fracture resistance, and have better centering ability, maintaining the shape of the original curved root canal and reducing the canal deviation. Examples of rotary systems: ProFile GT, ProFile Vortex, ProTaper Next, Reciproc, WaveOne.

Figure 5: Dentsply Protaper Next rotary system [20].

R phase

In 2008, SybronEndo developed an NiTi alloy by transforming a raw NiTi wire in the austenite phase into the R-phase through a thermal process. The thermomechanical treatment of NiTi alloy may create rearranged dislocation structures, making an instrument manufactured from the R-phase to be more flexible [12]. Examples of rotary systems: Twisted Files, k3 XF, TF Adaptive.

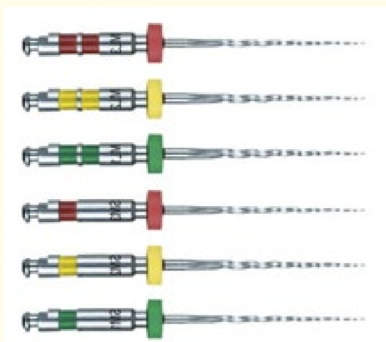

Figure 6: SybronEndo TF Adaptive Files rotary system [21].

CM wire (Control Memory-Wire)

CM NiTi files are manufactured with a special thermomechanical process that controls the material memory, making the files extremely flexible, but without the shape memory of other NiTi files. It has increased austenite transformation temperatures. The superior flexibility of CM Wire instruments is due to the fact that the maximum strain of CM Wire instruments before fracture (58.4%-84.7%) is much higher than that of the super-elastic ones

(16.7%-27.5%) [22]. The CM wire files can be prebend priour to their insertion into the root canal. Examples of rotary systems: Hyflex CM, ProDesign R, ProDesign Logic, Typhoon, M3 systems.

Figure 7: HyFlex CM rotary system [23].

Electrical discharge machining (EDM)

The technology was developed from CM wire by Coltène-Whaledent in 2016. When used to electrically conducting materials, EDM is a thermal erosion process that gives the instrument a crateriform surface finish. This NiTi alloy consists of martensite and substantial amounts of R-phase, exhibiting a significantly increased cyclic fatigue resistance [24]. Examples of rotary systems: HyFlex EDM, NeoNiTi, EDMax.

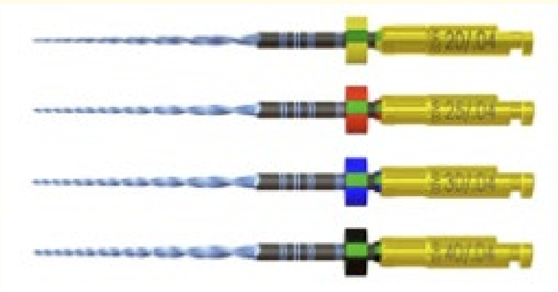

Figure 8: Edmax (EDM) rotary system [25].

Max-Wire (Martensite-Austenite-electropolish-filex). Introduced in 2015 by FKG, this is the first endodontic file system that combines both the shape memory effect and superelasticity in a single system in clinical applications [26]. The instrument can be in the martensitic phase at room temperature and return to the austenitic one when heated at a temperature above 35°C. Examples of rotary systems: XP-Endo-Finisher, XP-Endo-Shaper.

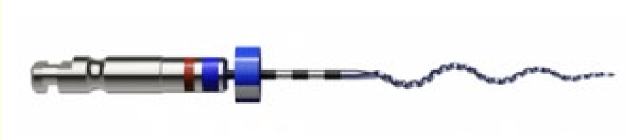

Figure 9: FKG- XP-Endo Shaper [27].

Blue wire and gold wire. Gold and blue heat treated NiTi files were introduced by Dentsply Sirona in 2012. The repeated heat and cooling treatments of the CM-wire alloy form a titanium oxide layer, of which surface color varies with the thickness of the titanium oxide layer: when the thickness is 60-80 nm, the surface color is blue, and when the thickness is 100-140 nm, the surface color is golden [28]. The cutting efficiency and wear resistance is increased by the presence of the titanium oxide layer. Examples of rotary systems: Vortex Blue, Reciproc blue, ProTaper Gold, WaveOne gold, Genius Proflex, ProTaper Ultimate. Genius Proflex system has different heat-treatments aiming to improve torsional fatigue resistance to small diameter files (purple surface color), and a better cyclic fatigue resistance to the big diameter files (gold surface color). ProTaper Ultimate system comprises instruments using three different heat-treated alloys: M-wire, Gold-wire and Blue heat-treated wire [29].

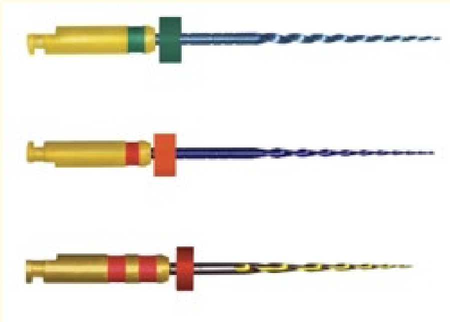

Figure 10: Genius Proflex rotary system [30].

All these consecutive metallurgical modifications targeted the improvements of the clinical behavior of endodontic instruments: better flexibility, maintaining the shape of the curved root canal, reducing canal transportation, enhance cyclic fatigue resistance of the instrument, reduce the risks of file separation due to torsional strain, and improve overall shaping abilities in the shorter period of time.

Another important aspect involved in the NiTi alloy behavior when used for the manufacturing of endodontic instruments consists in the need for different surface treatments. Due to challenges such as sudden fractures, low cutting efficiency and corrosion have prompted the need to resort to surface modifications to improve the performance of NiTi instruments.

Various surface modifications have been implemented to reduce or eliminate defects, increase surface stiffness or flexibility, improve cyclic fatigue resistance, and cutting efficiency.

The surface of NiTi endodontic instruments is usually characterized by the presence of titanium oxides (TiO_2), carbon, and oxygen. Much lower quantities of nickel oxides (NiO and Ni_2O_3) and metallic nickel could also be encountered.

The latest advancements include various surface treatment methods, including ion implantation, thermal nitridation, cryogenic treatment (CT), electropolishing, and physical or chemical vapor deposition [31].

Ion implantation

This coating technique has the role of minimizing the liberation of Ni from NiTi while preserving the mechanical properties.

- The implantation of nitrogen ions decreases the hardness of the instrument but increases resistance to wear, cutting efficiency, and cyclic fatigue resistance.
- The insertion of boron ions using a nonequilibrium technique substitutes nitrogen ions to achieve greater mechanical strength.

Thermal nitridation

This is a method for producing a surface layer that increases wear resistance and surface hardness. Heating to a temperature between 200 and 500°C in an nitrogen atmosphere leads to coating the NiTi files with a layer of titanium nitride (TiN), which significantly enhances the resistance to corrosion when immersed in sodium hypochlorite.

Cryogenic treatment

This technique has the role of increasing the surface hardness and thermal stability. It involves the immersion of the alloy in a super-cooled bath of liquid nitrogen at extremely low temperatures of around minus 196°C. Gradually warming to room temperature is then allowed. This method leads to improved cutting efficiency and strength of the instrument, influencing its whole cross-section, and not only the surface.

Electropolishing

This electrochemical process removes surface imperfections. The creation of a surface oxide layer improves corrosion and cyclic fatigue resistance, also diminishing the surface residual stress and making the endodontic file's surface smoother. Eliminating surface irregularities means an increased number of cycles until fracture (NCF) and fewer places of stress concentration that could lead to crack initiation and ultimately fracture [31].

Physical or chemical vapor deposition

This technique of coating is meant to form at low temperatures a thin layer of fine-grained titanium nitride film on the surface of NiTi endodontic files, leading to an increase of wear resistance, surface hardness, and cutting efficiency.

Conclusions

To achieve a successful endodontic treatment a few important aspects have to be taken into account.

The introduction of nickel titanium rotary instruments undeniably changed the way shaping root canal is performed.

The most obvious characteristics of the nickel titanium endodontic rotary instruments are related to their design features - such as taper, cross-section, flute/groove, cutting edges, radial land, pitch, tip, helix angle, rake angle - type of sequences, dynamics and kinematics - continuous or reciprocating rotation - and the speed and torque generated by the endo motor.

On the other hand, the properties of the NiTi alloy used for every rotary system are equally important. The key characteristics of NiTi instruments are their superelasticity and shape memory features which usually arise due the alloy's microstructural phase transformations. In fact, it must be remembered that every property concerning geometry, alloy type, and phase transformation temperatures of heat-treated NiTi rotary files affect their mechanical behavior.

All the advances concerning the NiTI alloy used in manufacturing the different generations of endodontic instruments have been based on the understanding of its behavior under real clinical conditions and on the capacity of the different heat treatments undertaken to improve every aspect of its physical properties implied in manufacturing better endodontic instruments.

Bibliography

1. Stanford materials.
2. A Brief History of Nitinol - Kellogg's Research Labs.
3. Andreasen GF and Hilleman TB. "An evaluation of 55 cobalt substituted Nitinol wire for use in orthodontics". *Journal of the American Dental Association* 82.6 (1971): 1373-1375.
4. Civjan S., *et al*. "Potential applications of certain nickel-titanium (nitinol) alloys". *Journal of Dental Research* 54.1 (1975): 89-96.
5. Walia HM., *et al*. "An initial investigation of the bending and torsional properties of Nitinol root canal files". *Journal of Endodontics* 14.7 (1988): 346-51.
6. do Martins JN. "Special Issue: Advances and Applications of Nickel-Titanium Alloys in Medical Fields, Special Issue Information". (2023).
7. Grande NM., *et al*. "A review of the latest developments in rotary NiTi technology and root canal preparation". *Australian Dental Journal* 68 (2023): S24-S38.
8. https://softroboticstoolkit.com/shape-memory-locomotion/design/coil-actuators
9. An Overview of the Nitinol (2023).
10. Wikimedia Commons, the free media repository.
11. Brotzu A., *et al*. "Chapter 3 - Standards for shape memory alloy applications, in Shape Memory Alloy Engineering, 2nd Ed Butterworth-Heinemann" (2021): 77-111.
12. Zupanc J., *et al*. "New thermomechanically treated NiTi alloys - a review". *International Endodontic Journal* 51.10 (2018): 1088-1103.
13. Liang Y and Yue L. "Evolution and development: engine-driven endodontic rotary nickel-titanium instruments". *International Journal of Oral Science* 14.1 (2022): 12.
14. Brantley WA., *et al*. "Differential scanning calorimetric studies of nickel titanium rotary endodontic instruments". *Journal of Endodontics* 28 (2002): 567-572.
15. Zanza A., *et al*. "Metallurgical Tests in Endodontics: A Narrative Review". *Bioengineering (Basel)* 9.1 (2022): 30.
16. Shen Y., *et al*. "Defects in nickel- titanium instruments after clinical use. Part 5: Single use from endodontic specialty practices". *Journal of Endodontics* 35 (2009): 1363-1367.
17. Azizi A., *et al*. "In-Depth Metallurgical and Microstructural Analysis of Oneshape and Heat Treated Onecurve Instruments". *European Endodontic Journal* 6.1 (2021): 90-97.
18. Generali L., *et al*. "Mechanical Properties and Metallurgical Features of New Green NiTi Reciprocating Instruments". *Materials* 13 (2020): 3736.
19. Quantec SC Niti Rotary Files Standard.
20. Dentsply Protaper Next.
21. SybronEndo TF Adaptive Files.
22. Agarwal S., *et al*. "NiTi Endodontics: Contemporary Views Reviewed". *Austin Journal of Dentistry* 5.4 (2018): 1112.
23. HyFlex CM.
24. Dablanca-Blanco A-B., *et al*. "Endodontic Rotary Files, What Should an Endodontist Know?" *Medicina* 58.6 (2022): 719.
25. Edmax (EDM) files.
26. Tabassum S., *et al*. "Nickel-Titanium Rotary File Systems: What's New?" *European Endodontic Journal* 4.3 (2019): 111-117.
27. FKG- XP-Endo Shaper.
28. Liang Y and Yue L. "Evolution and development: engine-driven endodontic rotary nickel-titanium instruments". *International Journal of Oral Science* 14 (2022): 12.
29. Martins JNR., *et al*. "Characterization of the file-specific heat-treated ProTaper Ultimate rotary system". *International Endodontic Journal* 56.4 (2023): 530-542.
30. Genius Proflex Intro Pack.
31. Agrawal PR., *et al*. "Revolutionizing endodontics: Advancements in nickel-titanium instrument surfaces". *Journal of Conservative Dentistry and Endodontics* 27.2 (2024): 126-133.