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Evolution of Nickel–titanium Alloys in Endodontics

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ABSTRACT

To improve clinical use of nickel–titanium (NiTi) endodontic rotary instruments by better understanding the alloys that compose them. A large number of engine-driven NiTi shaping instruments already exists on the market and newer generations are being introduced regularly. While emphasis is being put on design and technique, manufacturers are more discreet about alloy characteristics that dictate instrument behavior. Along with design and technique, alloy characteristics of endodontic instruments is one of the main variables affecting clinical performance. Modification in NiTi alloys is numerous and may yield improvements, but also drawbacks. Martensitic instruments seem to display better cyclic fatigue properties at the expense of surface hardness, prompting the need for surface treatments. On the contrary, such surface treatments may improve cutting efficiency but are detrimental to the gain in cyclic fatigue resistance. Although the design of the instrument is vital, it should in no way cloud the importance of the properties of the alloy and how they influence the clinical behavior of NiTi instruments.

Clinical significance: Dentists are mostly clinicians rather than engineers. With the advances in instrumentation design and alloys, they have an obligation to deal more intimately with engineering consideration to not only take advantage of their possibilities but also acknowledge their limitations.

Keywords: Cyclic fatigue, Endodontics, Martensitic alloys, M-wire, Nickel–titanium, Surface treatment, Torsional stress.

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INTRODUCTION

The endodontic treatment requires proper cleaning and shaping of the root canal space, i.e., removing tissues whether vital or necrotic and reducing the bacterial load in the case of infection, which is done through chemomechanical detersion protocols. To reach the apical part, practitioners have to improve the rheology of the root canal by giving it a continuously tapered shape. Until the early 1990s, this was conventionally done using stainless steel instruments that have a natural tendency to straighten curved canals when used in sizes 20/100 and above due to the inherent stiffness of the alloy and could not follow curvatures even in moderately curved canals. They had thus to be precurved to reach length, which in turn forced operators to use them exclusively in filing motion. This resulted in a high incidence of procedural errors, such as ledges, elbows, zipping, strippings, and perforations. Nickel–titanium alloys in dentistry[1] allowed for endodontic instruments that have reduced stiffness and increased elasticity, specifically engine-driven NiTi instruments that proved to be a valuable addition to the endodontic armamentarium. Since their introduction, these files have seen numerous improvements in not only file design and clinical sequences but also metallurgy. If modified clinical sequences and file design are relatively easy for practitioners to follow, modification in the alloys may prove more challenging and alloys designed to overcome a specific weakness may impact on another property of the alloy. This article presents an overview of the NiTi alloys currently used in endodontics.

About NiTi Smart Alloys

Nickel–titanium alloys (also known as NiTi or NITINOL for Naval Ordinance Laboratory) are known, when in nearly equiatomic proportions, to display an array of interesting properties, such as shape memory, superelasticity, and damping characteristics that arise from reversible crystallographic changes. It is noteworthy that a 0.1% change in composition will result in a 10°C change in the transformation temperature of the alloy and subsequently in its mechanical characteristics.[2] The NiTi alloys form Ni3Ti, NiTi, and NiTi2 intermetallic compounds. The nearly equiatomic NiTi alloy has broad compositional limits in the eutectoid phase field above 630°C, whereas Ni3Ti and NiTi2 are sharply defined compounds.[3] Below this temperature, a two-phase field (Ni3Ti, NiTi2) stretches between around 25 to 66% Ti. It is possible to preserve the metastable phase by cooling NiTi beneath this temperature.[4] When heated, NiTi displays a body-centered cubic structure, i.e., known as austenite. On cooling, a classic linear thermal contraction is visible until a certain limit [martensite start (Ms)] beyond which the contraction accelerates. This is caused by a progressive shear transformation to a monoclinic structure called martensite.[5] On further cooling, the contraction rate becomes linear again at a certain point [martensite finish (Mf)], pointing to the fact that the proportion of martensite phase in the alloy has reached 100%. Reheating this martensite will eventually reverse the process, yielding an austenite phase similarly an austenite start (As) and an austenite finish (Af) points. Generally, the As and Af temperatures are about 20°K above the Mf and Ms temperatures, signing the presence of a hysteresis phenomenon above the temperature transformation range.

A third rhombohedral phase or R-phase can also be described.[6,7] In general, it appears only on cooling before the martensitic transformation is complete. The face-centered cubic planar organization may be described as A, B, C, A, B, C…. It reflects the atoms' position in successive planes as compared with those in a randomly chosen reference plane. This organization involves a regular displacement of each plane in a specific direction. If the stacking sequence is reversed A, B, C, B, A, C… for instance, the crystal is said to be twinned. This happens in some alloys when compressive or tensile stresses are applied. It should be noted that the process is said to be nondiffusive and should happen atom by atom with every atom retaining all near-neighboring atom positions. The twinned martensite structure can hence, untwin on stress, but the load has to be nearly constant or slightly increasing. Furthermore, this untwinning is not an elastic strain: Atoms move from one energy minimum to another. This atom shifting phenomenon allows to absorb up to 8% of the strain as compared with the 0.1 to 0.2% strain limit of many other alloys.[3]

Conventional NiTi Alloys used in Endodontics

The main advantage of using NiTi alloys in root canal shaping instruments is the alloy's high flexibility.[8] Martensitic transformation can be stress induced from the austenitic phase over a narrow range of temperatures. Superelasticity occurs when a large reversible deformation occurs while increasing, stress appears to be constant (plateau). It happens as follows: Conventional NiTi alloys are in the austenite phase at body/room temperatures[9-11] Activation of austenitic NiTi produces an elastic deformation that follows a linear stress/strain function (the slope of the curve representing the elastic modulus). If deformation (stress) increases, the superelastic deformation appears, whereas strain remains constant. This superelastic behavior is a direct consequence of the martensitic transformation which occurs at the crystallographic level. The strain will remain constant until the entirety of the NiTi mass has shifted to the martensitic, which in turn will sign the end of the superelastic domain. Continuing the activation beyond that point will reveal conventional martensitic deformation with a classic linear stress/strain relationship as the crystallographic deformation's potential to absorb strain is exhausted.[8] Thus, if the load is relieved before reaching the plastic deformation limit, the deformation will be reversible, both ordinary austenitic elasticity and the pseudoelastic deformation due to phase change.

Again, as for thermal modification, the hysteresis phenomenon is present and the loading and unloading curves will not match. It is noteworthy that although the mechanism of action is similar, the aspect of stress–strain curves will vary significantly depending on the diameter of the wire, temperature, and annealing properties.[12] Having tested instruments from several manufacturers, Ounsi et al[13] established that the earlier generations of instruments were all manufactured from a unique 55%Ni–45%Ti. This becomes obvious when one considers that transformation temperatures of such alloys are highly sensitive to the composition and even 1% deviation in these percentages would almost yield a 100°C temperature threshold shift. As a direct consequence, melting plants must meet strict requirements in controlling nickel to titanium ratios to obtain the required final transformation temperatures.[14] Since NiTi alloys work harden rapidly, they cannot be cold-processed. Circular section wires are instead manufactured through die-drawing processes. For that, multiple reductions and frequent interpass annealing in the 600 to 800°C range are required to yield the required product.[15] When observed under scanning electron microscopy at high magnification, fractured surfaces of NiTi instruments revealed small voids regularly distributed throughout the bulk of the alloy.[16] They are due to the manufacturing process because when nickel and titanium ingots are melted together in a carbon crucible, there is a diffusion speed differential between the two elements inasmuch as the speed of diffusion of nickel atoms into the titanium ingot is different from that of titanium atoms inside the nickel ingot, which in turn creates voids known as Kirkendall porosities.[15] It is noteworthy that the distribution and size of these porosities reflect the specific metallurgical processing of the alloy.[17] These Kirkendall porosities seem to have an influence on the mechanical behavior of the alloy. Nagumo[18] hypothesized a hydrogen uptake into the alloy from oral liquids. This hydrogen would then move through interstitial sites, dislocations, and grain boundaries creating hydride phases that are responsible for hydrogen embrittlement. Asaoka et al[19] have reported that these hydride phases form primarily near the alloy surface. Furthermore, since the thickness of the subsequent brittle layer is variable, microcracks form on the surface when external forces induce deformation or abrasion. Thus, hydrogen adsorption is very likely to be an important factor in determining the lifespan of NiTi when subjected to biologic media.[19] It is unlikely that this would pose an issue during regular clinical use since there might not be sufficient time for the phenomenon to occur; however, it might become relevant during disinfection or sterilization protocols where the alloy would be in contact with ionized fluids for extended periods.

Thermal Treatments of NiTi Alloys

With the development of NiTi metallurgy to meet the requirement of endodontics, thermal processing is viewed today as the main approach to improving alloy properties by affecting its transition temperatures[20-23] and subsequently modifying fatigue resistance, whether torsional or cyclic. The thermal processes are obviously jealously guarded trade secrets and very little is known about them. They started with the Twisted Files from SybronEndo in 2007, which were produced by subjecting NiTi wires to several heat treatments. According to Gambarini et al,[24] file blanks are in the austenite phase before treatment. Then, when stress from the twisting process induces R-phase and martensitic transformation, a proprietary heat treatment is applied to maintain the crystallographic structure. This reportedly gives these files a higher fracture resistance than ground files.[25-27] The manufacturer further states that these files also have a different surface texture with a natural grain structure that runs longitudinally. These features reportedly serve to increase the flexibility and the fracture resistance of the instrument. Furthermore, since the instrument is twisted and surface treated, there is an absence of transverse-running machining marks, which results in slower crack initiation and propagation. Since R-phase alloy has a lower Young's modulus as compared with austenite, and would thus be more flexible.[11,28] From another standpoint, stress hysteresis is smaller for twisted and heat-treated instruments than it is for ground instruments.[11] This narrower hysteresis domain implies that more austenite is available for martensitic transformation when stress is applied,[29] which in turn translates into a higher fatigue resistance.[25,26,30,31] The year 2007 witnessed the introduction of M-wire (Sports Wire, Langley, OK). Since it is a thermally processed NiTi alloy, it is composed of a mixture of austenite and martensite phases stable at body temperature. The presence of the martensitic component improves the fatigue resistance properties of the file.[9,32-34] Differential scanning calorimetric examination established that conventional NiTi alloys displayed austenite structure at 37°C, whereas M-Wire showed nearly equal R-phase and austenite structures.[34] Another study[35] concluded that these heat-treated instruments exhibited higher cyclic fatigue resistance when compared with their conventional NiTi alloy counterparts. In addition, the twinned phase structure of M-wire allows it to absorb energy. This damping feature may prove, however, to be a disadvantage when using ultrasonics during file retrieval in the event of a file separation. Some heat-treated instruments also display a blue color due as a result of proprietary manufacturing processes that lead to a hard titanium oxide surface layer. This TiO layer compensates the loss of hardness resulting from the heat treatment, thereby improving wear resistance and cutting efficiency.[32] More recent heat-treated alloys are the controlled memory (CM) alloys, introduced in 2010. They generally have lower nickel content (52% wt.) and undergo special thermomechanical processes designed to maintain the extreme flexibility of the files and to eliminate the shape memory feature present in earlier alloys. Clinically, this would allow to prebend files before placing them in the canal, thus overcoming a major limitation of NiTi instruments that could not be previously prebent to conform to sharp root canal direction changes. Differential scanning calorimetry studies revealed that CM alloys had Af transition temperatures above 37°C, whereas the conventional NiTi alloys displayed Af transition temperatures below body temperature. Such results agree with previous studies that found that the conventional superelastic NiTi file had an austenite structure,[36-38] whereas as for M-wire, thermally processed CM alloys would mostly or totally be in the martensitic structure at body temperature.[21,39,40] Martensitic alloys deform easily and have the capacity to regain their original shape if heated above their transformation temperature. They do not, however, display the conventional stress-induced martensitic transformation observed in conventional NiTi alloys.[41] A major weakness of martensitic instruments is their higher tendency for permanent plastic deformation during instrumentation. Peters et al[42] reported that 82% of CM instruments plastically deformed after instrumentation with smaller size instruments having a higher tendency to plastically deform for a given torque value, and other instruments not regaining their original shape after the sterilization procedure. Due to these limitations, manufacturers recommend such instruments to be considered single use. It is noteworthy that even conventional (austenitic alloys) should not be used in more than four canals as the loss of cutting power would result in narrower shapes.[43] The NiTi instrument failure is generally due to several factors, namely the operator, the tooth, and the instrument, with the operator playing an important role. The operator's aptitude to feel and avoid the binding or screwing inside root canals is a skill that can be acquired and improved through experience.

Heat-treated NiTi instruments revealed significant microstructural phase changes of the alloy after clinical use.[44] When examining the apical part of new and deformed instruments, the shift from martensitic to austenitic was less after deformation. The authors attributed these differences to local stress variations during instrumentation. The tendency for heat-treated alloys to switch back from martensitic to austenitic under stress or when exposed to body temperature was also described in a recent paper in which the authors concluded that a significant proportion of heat-treated alloys (and thus supposed to be working in a martensitic phase) revert to austenitic as soon as they are exposed to body temperature.[45] On the contrary, the metallurgical characteristics of unused and clinically used heat-treated instruments did not seem to be affected by one single clinical use as no variation in the austenite-martensite phase transformation was detected in these instruments.[44]

Surface Treatment of NiTi Alloys

Since the alloy could not be changed at the time, alternative strategies to improving instrument behavior consisted in surface modification techniques that intend to avoid microcrack formation, which is a nucleation point leading to failure. The purpose was to enhance surface strength without changing bulk properties, such as superelasticity and toughness. One of these processes, electropolishing, is an electrochemical process that reduces surface irregularities (in contrast to electroplating where an electric current is used to deposit metallic ions onto one of the electrodes). The instrument is placed in a temperature-controlled electrolytic bath and connected to the positive terminal. When the direct current passes through the anode, the metal on the surface is oxidized and dissolved in the electrolyte. To electropolish a rough metallic surface, the extruding areas at the surface should be removed faster than depressions and surface imperfections due to the orientation of the crystals in a polycrystalline material should be suppressed without pitting. This is usually performed with specific ionic solutions and under rigorous (and generally proprietary) manufacturing control. This process is supposed to improve material properties, specifically fatigue and corrosion resistance; however, the evidence is controversial. Some authors[46,47] found an extension of fatigue life for electropolished instruments while most did not.[48-50] Moreover, Boessler et al[51] suggested a change in cutting behavior with an increase of torsional load after electropolishing; however, cyclic fatigue was reduced. One possible reason for these variations is the different testing environments used in these experiments. A recent paper testing the effect of electropolishing confirmed these facts and correlated the depth of the machining grooves to the variations in number of cycles to fracture: The deeper the grooves, the lower the fracture resistance.[52] Another approach to polishing is used for the twisted files (SybronEndo, Orange, CA, USA) and consists in treating the surface of the instrument with a proprietary Deox treatment. This Deox treatment appears to be similar to chemical polishing; the latter is typically done by subjecting the part to a cleaning solution (usually acidic) without the use of an electric current. As for electropolishing, there is little indication that chemical polishing would cause any effect on the mechanical properties of the underlying metal since the changes are limited to a few nanometers to a few micrometers from the very surface.[53] Physical vapor deposition is a process that allows coating of NiTi instruments with a layer of titanium nitride that confers a golden color to the surface of the instrument. The result is an improvement in cutting efficiency and corrosion resistance without affecting the superelastic properties.[54] Another process is plasma immersion or ionic ion implantation. It is obtained by changing the subsurface layer of the alloy using accelerated ions (plasma or ion gun) and was reported to increase the cutting efficiency without affecting the bulk characteristics of treated instruments.[55-58] Tripi et al[57] observed that nitrogen deposition would force elemental nickel from the surface inward, toward the core of instruments. This was corroborated by Alves-Claro et al.[59] However, one study showed that nitrogen ion implantation reflected negatively on the performance of such instruments when tested for fatigue. The authors attributed this negative file performance to nitrogen diffusing along grain boundaries instead of creating titanium nitride to surface harden the alloy.[60] Finally, one study considered boron implantation and reported that implanting boron into NiTi alloys had the potential of drastically improving cutting efficiency without hindering their superelastic properties.[61] Boron-implanted NiTi alloys had their surface hardness doubled when compared with pure Nitinol alloys at 0.05 μm depth. The surface hardness of this modified NiTi alloy exceeded that of stainless steel.[61] Finally, surface hardening can be achieved through cryogenic treatment.[62] The samples tested showed increased microhardness but no detectable change in crystalline phase composition or elemental composition. This was also confirmed by another study that concluded that deep dry cryogenic treatment "increases the cutting efficiency significantly but not the wear resistance."[63] A similar study was conducted pertaining to shape memory alloys.[64] It concluded that deep dry cryogenic treatment with 24 hours soaking period significantly reduced the hardness (and by extension reduced the likelihood for fracture), but it also reduced the wear resistance of shape memory NiTi alloys.

CONCLUSION

New alloys, NiTi or otherwise, are continuously introduced in endodontics. The alloy is but one of several variables affecting possible mishap occurrence during the instrumentation phase. Instrument design and root canal anatomy are also key variables affecting clinical performance. However, the most important variable remains the operator who is entrusted in handling the instruments. He or she should be just as much knowledgeable in the influence of alloy characteristics on the performance of the instrument they are using, as they should be regarding root canal anatomy or instrument design. This is key to ensure safety and efficiency during instrumentation.

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