REVIEW

An overview of nickel–titanium alloys used in dentistry

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Abstract

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Literature review The nickel–titanium alloy Nitinol has been used in the manufacture of endodontic instruments in recent years. Nitinol alloys have greater strength and a lower modulus of elasticity compared with stainless steel alloys. The super-elastic behaviour of Nitinol wires means that on unloading they return to their original shape following deformation. These properties are of interest in endodontology as they allow construction of root canal instruments that utilize these favourable characteristics to provide an advantage when preparing curved canals. This review aims to provide an overview of Nitinol alloys used in dentistry in order for its unique characteristics to be appreciated.

Keywords: endodontics, nickel–titanium, root canals.

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Introduction

In the early 1960s, a nickel–titanium alloy was developed by W. F. Buehler, a metallurgist investigating nonmagnetic, salt resisting, waterproof alloys for the space programme at the Naval Ordnance Laboratory in Silver Springs, Maryland, USA (Buehler *et al.* 1963). The thermodynamic properties of this intermetallic alloy were found to be capable of producing a shape memory effect when specific, controlled heat treatment was undertaken (Buehler *et al.* 1963). The alloy was named Nitinol, an acronym for the elements from which the material was composed; *ni* for nickel, *ti* for titanium and *nol* from the Naval Ordnance Laboratory. Nitinol is the name given to a family of intermetallic alloys of nickel and titanium which have been found to have unique properties of shape memory and super-elasticity.

The super-elastic behaviour of Nitinol wires means that on unloading they return to their original shape before deformation (Lee *et al.* 1988, Serene *et al.* 1995). As the alloy has greater strength and a lower modulus of elasticity compared with stainless steel (Andreasen & Morrow 1978, Andreasen *et al.* 1985, Walia *et al.* 1988), there may be an advantage in the use of NiTi instruments during the preparation of curved root canals, because the files will not be permanently deformed as easily as would happen with traditional alloys (Schäfer 1997).

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Metallurgy of nickel–titanium alloys

The nickel–titanium alloys used in root canal treatment contain approximately 56% (wt) nickel and 44% (wt) titanium. In some NiTi alloys, a small percentage (<2% wt) of nickel can be substituted by cobalt. The resultant combination is a one-to-one atomic ratio (equiatomic) of the major components and, as with other metallic systems, the alloy can exist in various crystallographic forms (Fig. 1). The generic term for these alloys is 55-Nitinol; they have an inherent ability to alter their type of atomic bonding which causes unique and significant changes in the mechanical properties and crystallographic arrangement of the alloy. These changes occur as a function of temperature and stress. The two unique features that are of relevance to clinical dentistry occur as a result of the austenite to

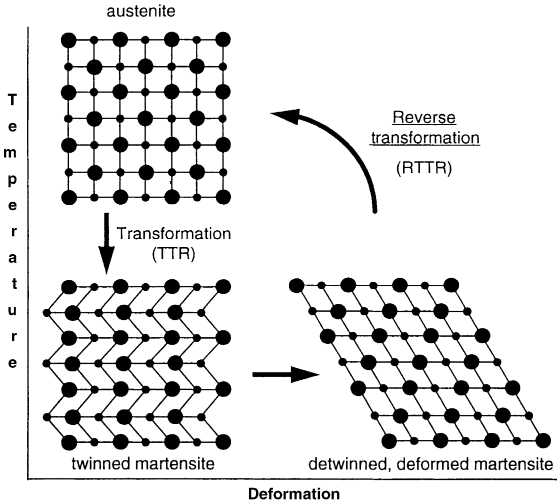

Figure 1 Diagrammatic representation of the martensitic transformation and shape memory effect of NiTi alloy.

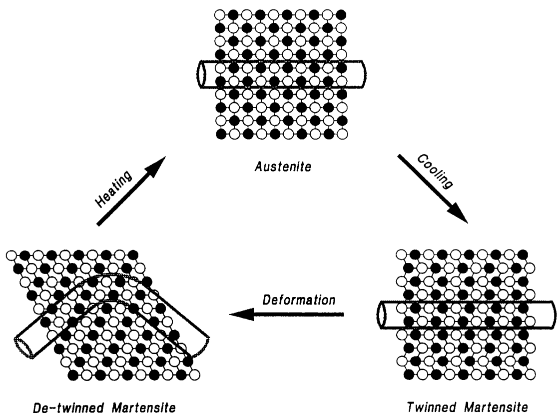

Figure 2 Diagrammatic representation of the shape memory effect of NiTi alloy.

martensite transition in the NiTi alloy; these characteristics are termed *shape memory* and *super-elasticity* (Figs 2 and 3).

Structure of nickel–titanium

The crystal structure of NiTi alloy at high temperature ranges (100 °C) is a stable, body-centred cubic lattice which is referred to as the *austenite phase* or parent phase (Fig. 1). Nitinol has the particular characteristic

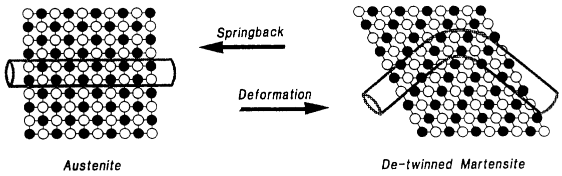

Figure 3 Diagrammatic representation of the super-elasticity effect of NiTi alloy.

that when it is cooled through a critical *transformation temperature range* (TTR), the alloy shows dramatic changes in its modulus of elasticity (stiffness), yield strength and electric resistivity as a result of changes in electron bonding. By reducing or cooling the temperature through this range, there is a change in the crystal structure which is known as the *martensitic transformation*; the amount of this transformation is a function of the start (Ms) and finish (Mf) temperature. The phenomenon causes a change in the physical properties of the alloy (Wang *et al.* 1972) and gives rise to the *shape memory* characteristic. The hysteresis of the martensitic transformation is shown in Fig. 4.

The transformation induced in the alloy occurs by a shear type of process to a phase called the *martensitic* or daughter phase (Fig. 1), which gives rise to *twinned martensite* (Fig. 1) that forms the structure of a closely packed hexagonal lattice (Fig. 1). Almost no macroscopic shape change is detectable on the transformation, unless there is application of an external force. The martensite shape can be deformed easily to a single orientation by a process known as de-twinning to *de-twinned martensite*, when there is a 'flipping over' type of shear. The NiTi alloy is more ductile in the martensitic phase than the austenite phase. The martensitic transformation and the shape memory effect is shown in Fig. 1.

The deformation can be reversed by heating the alloy above the TTR (reverse transformation temperature range or RTTR) with the result that the properties of the NiTi alloy revert back to their previous higher temperature values (Fig. 1). The alloy resumes the original parent structure and orientation as the body-centred cubic, high temperature phase termed *austenite* with a stable energy condition (Fig. 1). The total atomic movement between adjacent planes of atoms is less than a full interatomic distance when based on normal atomic lattice arrangements. This phenomenon is termed *shape memory* (Fig. 2) and allows the alloy to return to its

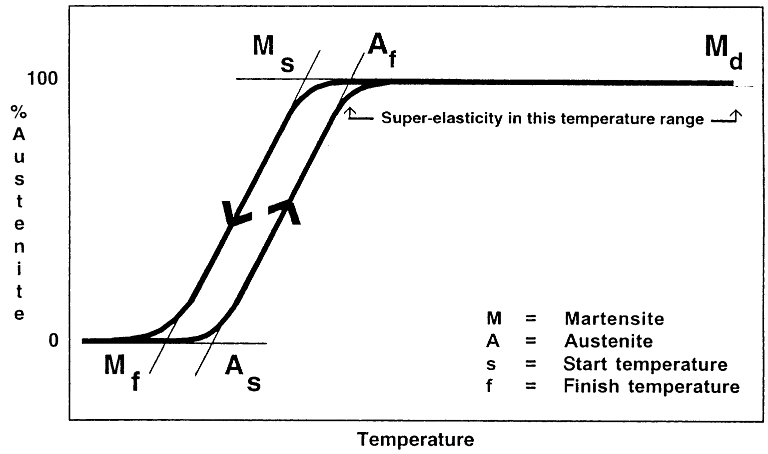

Figure 4 Hysteresis of martensitic transformation.

previous shape, by forming strong, directional and energetic electron bonds to pull back displaced atoms to their previous positions; the effect of this transformation is instantaneous.

It is possible using the shape memory effect to educate or place the NiTi alloy into a given configuration at a given temperature. This can be carried out at lower temperatures which deform the NiTi with a very low force and results in the 'twins' all occurring in the same direction. When the NiTi is heated through its transformation temperature it will recover its original 'permanent' shape (Fig. 2). The application of shape memory to orthodontics is discussed later. In terms of endodontology, this phenomenon may translate to the ability to remove any deformation within nickel–titanium instruments by heating them above 125 °C (Serene *et al.* 1995).

The transition temperature range for each nominal 55-Nitinol alloy depends upon its composition, as this causes considerable variability in the number of electrons available for bonding to occur and is constant for a particular NiTi alloy composition. The TTR of a 1 : 1 ratio of nickel and titanium is in the range of −50 to +100 °C. Reduction in the TTR can be achieved in several ways; in the manufacturing process both cold working and thermal treatment can significantly affect TTR, as can altering the nickel : titanium ratio in favour of excess nickel or by substituting cobalt for nickel, atom for atom. Cobalt substitution produces alloys with the composition $NiTi_xCo_{1-x}$. The TTR can be lowered progressively by continued substitution of cobalt for nickel as cobalt possesses one less electron than nickel, thus lowering the total number of bonding electrons. However, formation of a detrimental second phase $NiTi_3$ occurs if excess nickel is added in attempts to lower the TTR.

Stress-induced martensitic transformation

The transition from the austensitic to martensitic phase can also occur as a result of the application of stress, such as occurs during root canal preparation. In most metals, when an external force exceeds a given amount mechanical slip is induced within the lattice causing permanent deformation; however, with NiTi alloys a *stress-induced martensitic transformation* occurs, rather than slip. This causes:

- a volumetric change associated with the transition from one phase to the other and an orientation relation is developed between the phases
- the rate of the increase in stress to level off due to progressive deformation (Fig. 5) even if strain is added due to the martensitic transformation. This results in the so-called *super-elasticity* (Fig. 4), a movement which is similar to slip deformation. The differences between the tensile behaviours of NiTi and stainless steel alloy can be seen in Fig. 6.
- *springback* when the stress decreases or stops without permanent deformation occurring (Fig. 3). Springback is defined as load per change in deflection (Andreasen & Morrow 1978), to the previous shape with a return to the austenite phase, provided the temperature is within a specific range (Fig. 4).

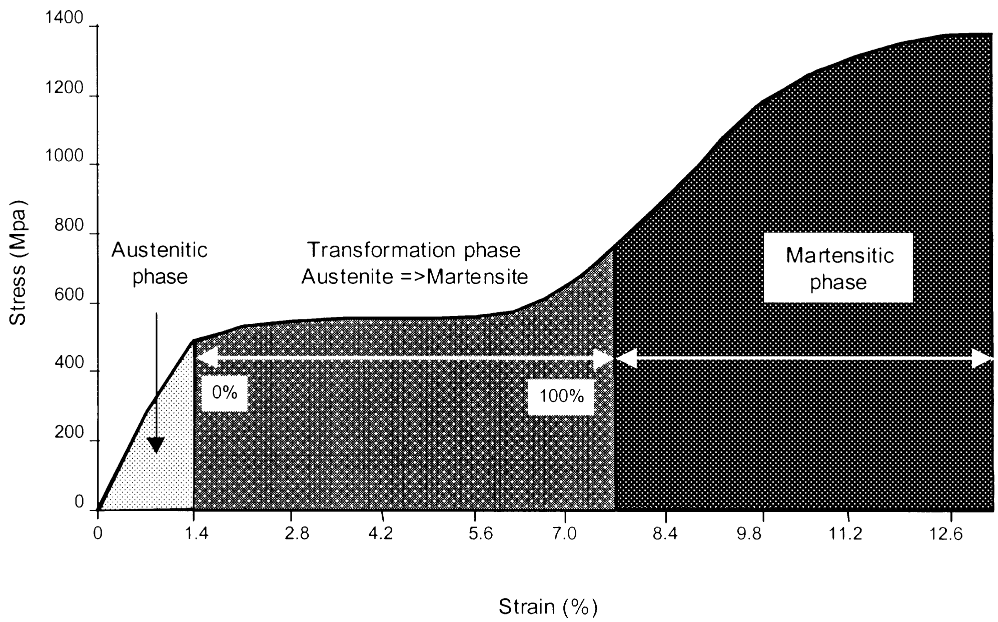

Figure 5 NiTi phase transformation.

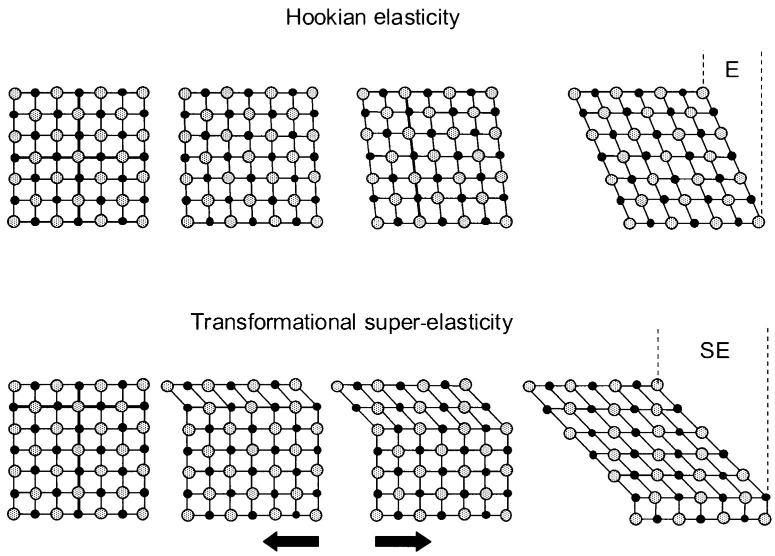

Figure 6 Diagrammatic representation of the tensile behaviour of stainless steel and NiTi super-elastic alloy and mechanisms of elastic deformation.

The plastic deformation that occurs in NiTi alloys within or below the TTR is recoverable, within certain limits, on reverse transformation. It is this phenomenon of crystalline change which gives rise to the shape memory effect of the material and the super-elastic behaviour. The part of the RTTR in which *'shape recovery'* occurs is termed the *shape recovery temperature range* (SRTR). This has also been termed 'mechanical memory' (Buehler & Wang 1968). This is unlike conventional metallic stress-strain behaviour where elastic response in conventional alloys is recoverable, but is small in size; and where larger strains are associated with plastic deformation, that is not recoverable (Fig. 7).

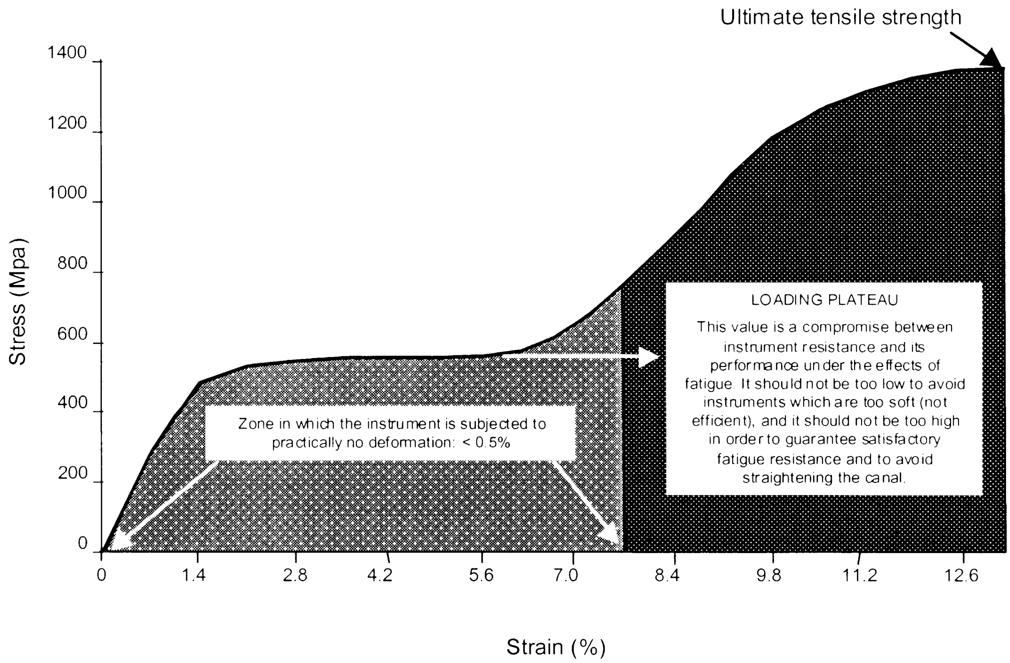

Figure 7 NiTi strength curve.

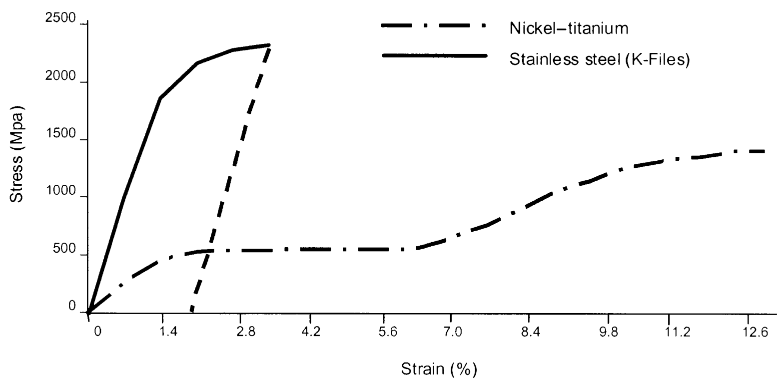

Figure 8 Stress-strain curve: stainless steel and nickel–titanium.

The super-elasticity of nickel–titanium allows deformations of as much as 8% strain to be fully recoverable (Fig. 8), in comparison with a maximum of less than 1% with other alloys, such as stainless steel. Although other alloys such as copper–zinc, copper–aluminium, gold–cadmium and nickel–niobium have been found to have super-elastic properties (Buehler & Wang 1968), nickel–titanium is the most biocompatible material and has excellent resistance to corrosion.

An alloy system is an aggregate of two or more metals which can occur in all possible combinations. As such, a second group of Nitinol alloys can be formed if the NiTi alloy contains more nickel and as this approaches 60% (wt) Ni an alloy known as 60-Nitinol forms. The shape memory effect of this alloy is lower, although its ability to be heat-treated increases. Both 55 and 60-Nitinols are more resilient, tougher and have a lower modulus of elasticity than other alloys such as stainless steel, Ni–Cr or Co–Cr (Fig. 8). Table 1 shows the values for typical properties of Nitinol alloys.

Table 1 Typical properties of Nitinol alloys

Property	55-Nitinol austenite	55-Nitinol martensite
Physical		
Density (gm cm^3)	6.45	
Melting point (°C)	1310	
Magnetic permeability	<1.002	
Coefficient of thermal expansion ($\times 10^6$/°C)	11.0	6.6
Electrical resistivity (ohm-cm)	100×10^{-6}	80×10^{-6}
Hardness 950 °C (Furnace cooled)	89 R_B	
Hardness 950 °C (Quenched-R.T. water)	89 R_B	
Mechanical		
Young's modulus (Gpa)	120	50
Yield strength (Mpa)	379	138
Ultimate tensile strength (Mpa)	690–1380	
Elongation	13–40%	
Shape memory		
Transformation temperature (°C)	−50 to +100	
Latent heat of transformation	10.4 BTU lb^{-1}	
Shape memory recoverable strain	6.5–8.5%	
Super-elastic recoverable strain	up to 8%	
Transformation fatigue life	several hundred	
at 6% strain	cycles	
at 2% strain	10^5cycles	
at 0.5% strain	10^7cycles	

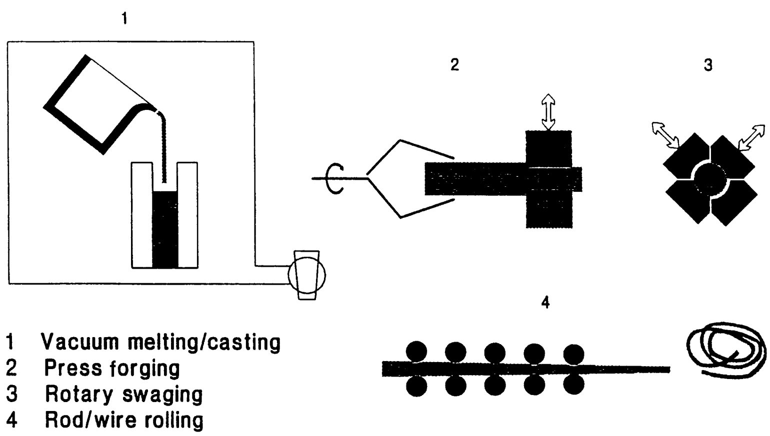

Figure 9 Diagrammatic representation of the manufacturing process of Nitinol alloy.

Manufacture of Nitinol alloy

Nickel–titanium alloy production is a very complex process that consists of:

- vacuum melting/casting
- press forging
- rotary swaging
- rod/wire rolling

In the past, NiTi alloys with near stoichiometric composition have been produced satisfactorily by both arc and induction melting methods (Buehler & Wang 1968). One of the problems encountered with arc-melting was that it required multiple remelts to ensure chemical homogeneity; however, importantly this process produces only minimum contamination of the alloy. Current manufacture involves the use of vacuum induction melting in graphite crucibles (Fig. 9) that ensures effective alloy mixing by simple means, with slight carbon contamination in the melt forming TiC (Buehler & Cross 1969). The presence of oxide impurities does not effect the unique properties of 55-Nitinol, as these appear to be evenly distributed within the NiTi matrix.

The double vacuum melting manufacturing process ensures purity and quality and maintains the mechanical properties of the alloy. The raw materials are carefully formulated before the alloy is melted by vacuum induction. After this process, vacuum arc remelting takes place to improve the alloy chemistry, homogeneity and structure. The double melted ingots are hot worked and then cold worked to a variety of shapes and sizes according to product specifications, i.e. Nitinol wires, bars, etc. as described earlier. Alloys for orthodontic or medical use can be produced as drawn or with mechanically cleaned surfaces.

Hot and cold working can be undertaken on Nitinol alloys, below the crystallization temperature. The alloy composition is important to the manufacturing process and it appears that 55-Nitinol can be processed by all forms of hot working more easily than 60-Nitinol. Strengthening of the alloy occurs through low temperature deformation and maintains a minimum of 12% tensile elongation. Some NiTi alloys appear to be sensitive to the effects of heat treatment that can effect both shape memory and the pseudo-elastic behaviour; however, NiTi alloys of near stoichiometric composition such as are used in dentistry do not appear to be affected (Saburi *et al*. 1982, Mercier & Torok 1982).

Gould (1963) studied the machining characteristics of nickel–titanium alloys and found that tool wear was rapid and the cutting speed, feed, tool material, tool geometry and type of cutting fluid had an effect on the results of the manufactured Nitinol. Specifically, these alloys could be turned 10–20 times faster with carbide tools than with high speed steel tools. Light feeds of 0.003–0.005 in rev^{-1} are recommended in turning Gould 1963) and in order to maximize the tool life, 55-Nitinol should be cut at a speed of 220 ft min^{-1}. An active highly chlorinated cutting oil is advised to obtain a reasonable drill-life along with the use of silicon carbide wheels to grind the surface of Nitinol alloys. The speeds at which cutting tools should be operated vary according to the composition of the alloy. Therefore, it appears that sharp carbide cutting tools are required to machine Nitinol alloys using techniques involving light feeds and slow speeds.

Construction of root canal instruments

The manufacture of NiTi endodontic instruments is more complex than that of stainless steel instruments, as the files have to be machined rather than twisted. The super-elasticity of the alloy means that it cannot maintain a spiral as the alloy undergoes no permanent deformation. Attempts to twist instruments in a conventional way would probably result in instrument fracture (Schäfer 1997). The instrument profile (design) has to be ground into the Nitinol blanks. Further difficulties during production include elimination of surface irregularities (milling marks) and metal flash (roll-over) on the cutting edges that may compromise the cutting ability of these instruments and potentially cause problems with corrosion (Fig. 10).

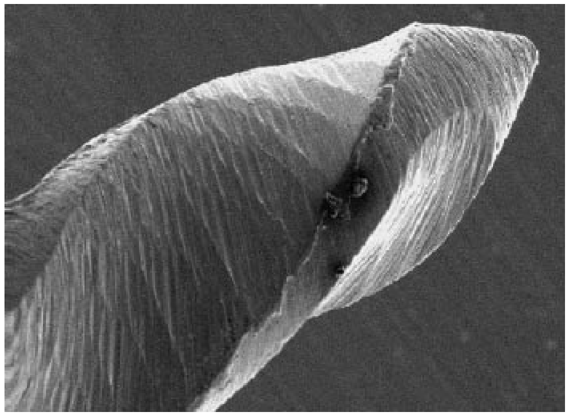

Figure 10 SEM photomicrograph of milling marks and roll-over on a rotary NiTi instrument.

The composition of Nitinol used to construct endodontic instruments is 56% (wt) nickel and 44% (wt) titanium. Although only one manufacturer (Dentsply, Maillefer Instruments SA, Ballaigues, Switzerland) has released the absolute composition and manufacturing details of the nickel–titanium used to construct their instruments, it would appear that this is the only alloy composition that can utilize the super-elastic properties of the alloy.

It is possible to vary the composition of NiTi alloy in order to give rise to wires with two different characteristics; either to be a super-elastic alloy or to have the shape memory property. The differences between the alloys are in their nickel content and the transitional temperature range for the given alloy. Various parameters affect the transformation temperature; a decrease in the transformation temperature occurs with an increase in nickel content or by substituting trace elements such as cobalt as discussed previously, whilst an increase in annealing temperature increases the transformation temperature. Ideally, for the manufacture of root canal instruments the ultimate tensile strength of the alloy should be as high as possible to resist separation (Fig. 7), whilst the elongation parameters must be suitable for instrument

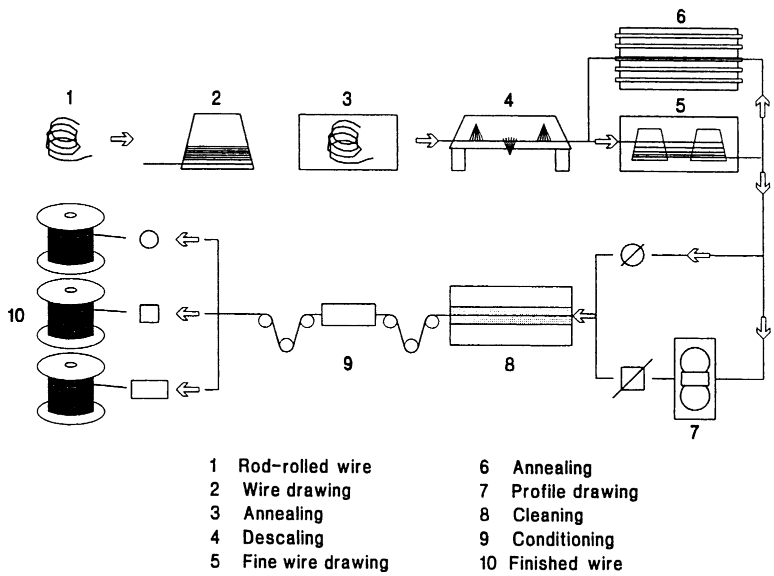

Figure 11 Diagrammatic representation of the production of finished Nitinol wire.

flexibility, (Fig. 8) thereby decreasing canal transportation, and to allow high resistance to fatigue.

Once the alloy has been manufactured, it undergoes various processes before the finished wire can be machined into a root canal instrument (Fig. 11). Essentially, the casting is forged in a press into a cylindrical shape prior to rotary swaging under pressure, to create a drawn wire. The wire is then rolled to form a tapered shape with even pressure from a series of rollers applied to the wire. During the construction phase, other processes are carried out on the rod-rolled wire including drawing the wire onto a cone, annealing the wire in its coiled state, descaling and further fine wire drawing followed by repeated annealing with the wire in a straight configuration. This stage is followed by drawing the actual profile or cross-sectional shape of the wire, e.g. imparting either a round, square or oblong shape prior to a cleaning and conditioning process. The finished wire is stored on reels prior to machining. This process is illustrated in Fig. 11.

Uses of nickel–titanium alloy

Nitinol wire was first used in the self-erectile action of a disc on rod antenna that recovered its prefolded shape above the transition temperature of the alloy (Buehler & Wang 1968). The unique 'mechanical memory' of 55-Nitinol allowed it to recover its original shape after mechanical distortion by heating it above the transition temperature. The rate of recovery of the antenna was determined by the rate at which the critical temperature was reached, which depended on the thermal conductivity and the mass of the material. The corrosion resistance of Nitinol alloys was evaluated by Buehler & Wang (1968) who reported that they performed adequately in a marine environment.

Duerig (1990) described applications for shape memory NiTi alloys grouped according to the primary function of the memory element. An example of (i) *free recovery* was NiTi eyeglass frames, (ii) *constrained recovery* was couplings for joining aircraft hydraulic tubing and electrical connectors, (iii) *work production* was actuators both electrical and thermal and (iv) *super-elasticity* was orthodontic archwire, guidewires and suture anchors.

Further uses of the super-elastic properties of NiTi wire were described by Stoeckel & Yu (1991). As super-elasticity is an isothermal event, applications with a well controlled temperature environment are most successful, e.g. in the human body. NiTi wire has been used as orthodontic archwire and springs, in Mammalok® needle wire localizers (to locate and mark breast tumours), guidewires for catheters, suture needles and anchors, the temples and bridges for eyeglasses, and, in Japan, underwire brassieres.

Use of nickel–titanium alloys in dentistry

Orthodontics

Initially NiTi alloys were used in the construction of orthodonic archwires. Extensive research published in the materials science and orthodontic journals has allowed the properties of the material to be appreciated and used in an appropriate clinical manner. Many of these studies have relevance to an understanding of NiTi alloys used in endodontology and a brief description of this literature is described.

NiTi wires were first used in orthodontics by Andreasen & Hilleman (1971), who observed differences in the physical properties of Nitinol and stainless steel orthodontic wires that allowed lighter forces to be used. The strength and resilience of NiTi wires meant there was a reduction in the number of arch wire changes necessary to complete treatment. Rotations of teeth could be accomplished in a shorter time, without increasing patient discomfort. Nitinol wires showed better resistance to corrosion so were felt more appropriate for intraoral use than stainless steel.

Andreasen & Morrow (1978) observed the unique properties of Nitinol, including its outstanding elasticity (which allows it to be drawn into high-strength wires) and its 'shape memory' (which allows the wire when deformed, to 'remember' its shape and return to its original configuration). The most important benefits of Nitinol wire were its construction as a resilient, rectangular wire that allowed simultaneous rotation, levelling, tipping and torquing movements, to be accomplished early in treatment. Limitations to the use of the material were noted, such as the time taken to bend the wires, the necessity of not using sharp-cornered instruments that could lead to breakage and the inability to be soldered or welded to itself. Overall, the authors felt the material represented a significant improvement over conventional arch wire and was a valuable addition to the orthodontist's armamentarium.

Burstone & Goldberg (1980) observed beneficial characteristics such as low modulus of elasticity combined with a high tensile strength that allowed wires to sustain large elastic deflections due to the very high springback quality. Limitations such as restricted formability and the decrease of springback after bending prompted investigations into other alloys, such as beta titanium. Drake *et al.* (1982) concluded that Nitinol wire was suitable mainly for pretorqued, preanglulated brackets.

Miura *et al.* (1986) tested a new Japanese NiTi alloy and compared it to stainless steel, Co–Cr–Ni and Nitinol wires. Japanese NiTi alloy exhibited super-elastic properties and was least likely to undergo permanent deformation during activation. The Nitinol wire showed less permanent deformation and excellent springback qualities in comparison with the stainless steel and Co–Cr–Ni wires, however, load and deflection were almost proportional, indicating lack of super-elastic qualities. This may have been due to the fact that Nitinol was manufactured by a work-hardening process, thus affecting the properties of shape memory or super-elasticity.

Kusy & Stush (1987) observed a discrepancy between the stated dimensions of wires of 10 Nitinol and seven beta titanium wires; the sizes were smaller 95% of the time and neither wire obeyed simple yield strength relationships. The ultimate tensile strength of Nitinol wires increased with decreasing cross-sectional area and also appeared more ductile with increasing cross-sectional area.

Yoneyama *et al.* (1992) assessed the super-elasticity and thermal behaviour of 20 commercial NiTi orthodontic arch wires. A three-point bending test allowed load-deflection curves to be determined and differential scanning calorimetry was used to determine thermal behaviour due to phase transformation of the alloy. Substantial differences were noted between the wires; some showed super-elasticity (which occurs with the stress induced martensitic transformation), whilst other wires only had good springback qualities. Super-elasticity was only exhibited by wires showing high endothermic energy in the reverse transformation from the martensitic phase to the parent phase and with low load/deflection ratios. These wires showed nearly constant forces in the unloading process, a desirable physiological property for orthodontic tooth movement; the lower the L/D ratio, the less changeable is the force which the wire can display.

Clearly, there are differences in the mechanical properties and thermal behaviour of NiTi alloy which vary with composition, machining characteristics and differences in heat treatment during manufacture. The need for correct production of NiTi alloys was stressed by Yoneyama *et al.* (1992) in order that the desired clinical characteristics could be obtained.

Evans & Durning (1996) reported the differences in formulations of nickel–titanium alloy and their applications in archwire technology. A review article published by Kusy (1997) described the properties and characteristics of contemporary archwires from initial development to their current use in variable modulus orthodontics as advocated by Burstone (1981). The variation in composition of nickel–titanium alloys was discussed together with the influence this had on the properties of the resultant alloy.

Corrosion behaviour of NiTi orthodontic wires

The corrosion behaviour of Nitinol orthodontic wires was compared with stainless steel, cobalt-chrome and β-titanium by Sarkar *et al.* (1979). The wires were exposed to a 1% NaCl solution via an electrochemical cyclic polarization technique. Scanning electron microscopy and energy dispersive X-ray analysis was used to determine differences between pre- and postpolarized surfaces. The Nitinol alloy was the only specimen to exhibit a pitting type corrosion attack, which the authors concluded warranted further investigation.

Sarkar & Schwaninger (1980) studied the *in vivo* corrosion characteristics of seven Nitinol wires in clinical use for 3 weeks to 5 months. Scanning electron microscopy revealed the presence of numerous, round-bottomed, corrosion pits interspersed with corrosion products rich in titanium. This was presumed to be a mixed oxide of titanium and nickel. Fractured surfaces of Nitinol wires showed small equiaxed dimples that resulted from microvoid coalescence within the grain-boundary zones. There appears to be correlation with *in vitro* (Sarkar *et al.* 1979) and *in vivo* corrosion of Nitinol.

The performance of wires used in orthodontics can be affected by corrosion in the mouth. Edie & Andreasen (1980) examined Nitinol wires under SEM as received from the manufacturer and following 1 month to 1 year's use in the mouth. They found no corrosion of the Nitinol wires with maintenance of a smooth, undulating surface. In contrast, stainless steel wires showed sharp elevations of metal particles on their surface.

Clinard *et al.* (1981) used polarization resistance and zero resistance ammetry to study the corrosion behaviour of stainless steel, cobalt–chromium, beta-titanium and Nitinol orthodontic springs. They also studied the effect of coupling the wires to stainless steel brackets. In orthodontic treatment, the corrosion behaviour of the wires was affected by coupling to the brackets. The effects of beta-titanium and cobalt–chromium were comparable showing less corrosion than the other wires, however, Nitinol was shown to be inferior to stainless steel, with a tendency to pitting attack. The authors concluded that over the relatively short period of orthodontic treatment, the effect of the corrosion did not appear to be deleterious to the mechanical properties of the wires, and should not significantly effect the outcome of treatment.

To assess corrosion potential, Edie *et al.* (1981) compared Nitinol wire with stainless steel wire in clinical use for periods ranging from 1 to 8 months. Scanning electron microscopy was used to assess surface characteristics; qualitative chemical information was obtained with X-ray spectrometry to indicate oxide prevalence and organic contamination of the wires. Unused Nitinol wires exhibited large variations in surface texture with an undulating 'bubbling' or mottled 'caked' appearance In comparison, stainless steel wires were generally smoother, but showed small metallic prominences. Obvious pits occurred on electrolytically corroded Nitinol wires, with loosely bound corrosion products; however, after clinical use, no differences in surface characteristics were obvious when comparing pre- and postoperative SEM photographs. There was no significant difference between the surface oxygen content of Nitinol compared to stainless steel, which would suggest that there were no differences in the clinical performance of the two wires, in terms of corrosion.

Effects of sterilization on NiTi orthodontic wires

Mayhew & Kusy (1988) examined the effects of dry heat, formaldehyde-alcohol vapour and steam autoclave sterilization on the mechanical properties and surface topography of two different nickel–titanium arch wires. The wires were being reused clinically, due to their high cost. After sterilization, the elastic modulus and tensile properties were determined for Nitinol and Titanal wires (Lancer Pacific, Carlsbad, CA, USA); laser scanning was employed to detect surface alterations caused by tarnish, corrosion or pitting.

No detrimental effects were noted, and the nickel–titanium arch wires maintained their elastic properties, had excellent resilience and low load-deflection rates, which led the authors to conclude that stabilized martensitic alloys such as Nitinol could be heat sterilized, without forming tempered martensite. The specular reflectivity for Nitinol was determined by laser spectroscopy and ranged from 1.1 to 4.6 μ W. Sterilization did not appear to effect surface topography adversely.

The load-deflection characteristics of NiTi wires after clinical recycling and dry heat sterilization were examined by Kapila *et al.* (1992). Thirty 0.016 inch work-hardened Nitinol and austensitic NiTi wires were subjected to a three-point bending test in an 'as received' condition, and after one and two cycles of dry heat sterilization for 5 min at temperatures that ranged from 203 to 217 °C. It was observed that recycling these wires after sterilization causes significant changes to the loading and unloading forces associated with the wires, together with a reduction in the pseudo-elasticity of NiTi wires and an increase in the stiffness of both the Nitinol and NiTi wires.

Three types of nickel–titanium wires, a β-titanium and a stainless steel wire were sterilized by either cold, dry or steam autoclave sterilization by Smith *et al.* (1992). A transverse load test, tensile strength and corrosion resistance test was carried out on 40 wires of each type used clinically for 1–6 months and on five wires in an as received condition. There were no clinically significant differences between the new or previously used NiTi wires.

Other uses of nickel–titanium alloy in dentistry

Castings for crowns and denture construction

The use of NiTi alloy in the construction of dental prostheses was first investigated by Civjan *et al.* (1975) who cast 55-Nitinol into phosphate-bonded investment moulds. However, castings of tensile bars, inlays and crowns were found to be rough, brittle and devoid of mechanical memory. The shape memory properties of the alloy were investigated for construction of partial denture clasps. It proved difficult to adapt Nitinol wires to the cast, overbending was necessary and resilience was lost in fixing the shape; however, shape recovery occurred within 2–5 s in the mouth and was improved on further warming.

Difficulties have been encountered in casting NiTi alloy using conventional dental casting techniques with loss of the inherent special properties of NiTi alloy in the casting process. Titanium is very reactive at high temperatures and the mechanical properties and surface conditions can be influenced by the mould materials. Hamanaka *et al.* (1985) used graphite coating on phosphate bonded investments in a new casting machine and observed a noticeable decrease in the reaction between NiTi alloys and the phosphate bonded investment.

The use of NiTi alloy for prefabricated straight-slit type posts was studied by Hasegawa (1989). It appeared that NiTi alloy could be processed without loss of the shape memory effect by an electric discharge machining and that retention forces after cementing was similar or stronger with the NiTi trial posts than with other posts. The cementation pressure of the NiTi post into the root canal filled with unset cement was low.

In a later study, Hasegawa (1991) compared differences in NiTi alloy structure on the influence of stress on post crown preparations. Threaded posts were constructed above the transformation point and were found to cause twice as much stress as posts constructed below that point. At temperatures of 35 °C NiTi posts made of the martensitic structure caused less stress than posts made of the austenite structure. No differences were noted between the two NiTi structures in influencing the thickness of the cement lute.

Construction of implants

To take advantage of the shape memory characteristics of the alloy, NiTi alloy was used for fabrication of endosseous blade type implants (Sachdeva *et al.* 1990). The ability to enhance the adhesiveness of nickel–titanium implants to bone was investigated by Kimura & Sohmura (1987) who sprayed the surface of both NiTi alloy and titanium alloy with Ti, by a plasma thermal spray under argon gas atmosphere. A pure Ti layer was formed after spraying, however, a 5–10 μm crevice was noted between the coated layer and the matrix metal and dissolution of the coated layer was detected when the material was placed in 1% NaCl solution.

It appeared that if the specimens were vacuum annealed at 950 °C for 1–1.5 h the crevice disappeared, forming a bonded layer with a composition corresponding to Ti_2-Ni on the Ti-Ni matrix. Closer adhesion and corrosion resistance was achieved with the Ti specimen. Kimura & Sohmura (1987) felt that a thinner coating of Ti or an application of Ti_2-Ni alloy phase would be worth investigating, to avoid the coated layer peeling off when large strains were placed on the shape memory alloy.

Kimura & Sohmura (1988) studied the effects of coating NiTi implants with oxide film to decrease the dissolution of Ni in 1% NaCl solution. The corrosion resistance was measured by anodic polarization measurements; the effect of the oxide film was to suppress dissolution at low potentials. On repeated polarization, a further decrease in current density was observed as a result of stabilization of the passive state on the surface. The oxide film adhered closely to the matrix without peeling or cracking by the plastic deformation associated with the shape memory effect. The effect of scratching the oxide surface did not cause dissolution at low potential, therefore maintaining a stable surface.

Sachdeva *et al.* (1990) described the applications of shape memory NiTi alloys in dentistry and reported that over 5000 NiTi blade implants had been used on patients in Japan. The implant blades were trained to open at a temperature of 50 °C in order to allow greater stability of the implant. After insertion, the implant was irrigated by warm saline and, more recently, by an induction coil apparatus. No adverse reports of nickel hypersensitivity have been reported.

Oral surgery

Schettler *et al.* (1979) investigated the construction of NiTi alloy bone plates to act as alveolar bracing and counteract the effects of mastication during bony repair in the treatment of transverse mandibular fractures. As a result of the shape memory effect, the NiTi alloy assumed its original shape after repeated deformation and produced higher compressive strengths.

Kuo *et al.* (1989) described the use of nickel–titanium alloy in China, for 71 cases of orthopaedic surgery and 265 clinical cases ranging from maxillofacial correction to fallopian tube clamping. Nitalloy (56% nickel and 44% titanium, manufactured in Shanghai, China) was compared with Nitinol (55% nickel and 45% titanium from USA) and other materials in common orthopaedic use; 316 L stainless steel, Co–Cr–Mo alloy, pure titanium and Ti6Al4V alloy. Nitalloy showed superior results for modulus of elasticity, yield and shear strength, elongation ratio and fatigue limit. Miura *et al.* (1990) described the applications of super-elastic NiTi rectangular wire in combined surgical–orthodontic treatment.

Conclusion

Because of their super-elasticity, nickel–titanium alloys are being used increasingly in the construction of endodontic instruments. It is important for clinicians to be aware of the metallurgy of NiTi alloy in order that the characteristics of instruments constructed from this alloy can be appreciated and to encourage research to maximize their clinical potential. This review attempted to highlight the various uses of NiTi alloy in dentistry and previous research findings that may have relevance to endodontology.

Whilst NiTi root canal instruments are more flexible than stainless steel files and have the ability to prepare canals quickly and without undue aberrations (Esposito & Cunningham 1995, Glosson *et al.* 1995, Thompson & Dummer 1997a, 1997b, 1997c, 1997d, 1997e, 1997f, 1998a, 1998b, 1998c, 1998d, Bryant *et al.* 1998a,b), there are important considerations such as their increased cost, the potential decrease in cutting ability due to wear (Walia *et al.* 1989, Schäfer *et al.* 1995) and the ability to machine instruments with various designs and dimensions to a consistent size (Marsicovetere *et al.* 1996). These issues need to be addressed so that endodontists can embrace the use of instruments constructed from this new alloy with confidence. Clearly, the effects of sterilization and corrosion during clinical use on NiTi alloys needs to be examined more closely, together with the enhancement of their hardness by ion implantation (Lee *et al.* 1996).

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