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).

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

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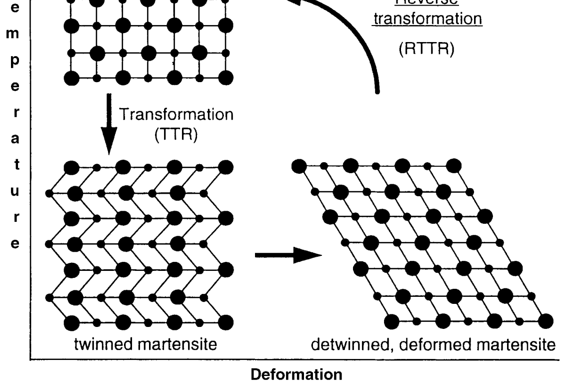

Figure 1 Diagrammatic representation of the martensitic transformation and shape memory effect of NiTi alloy.

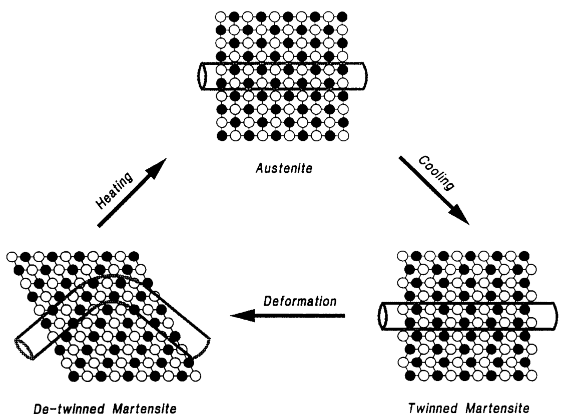

Figure 2 Diagrammatic representation of the shape memory effect of NiTi alloy.

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

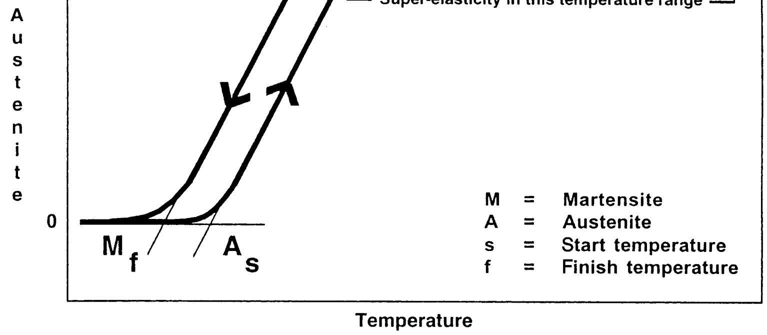

Figure 4 Hysteresis of martensitic transformation.

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).

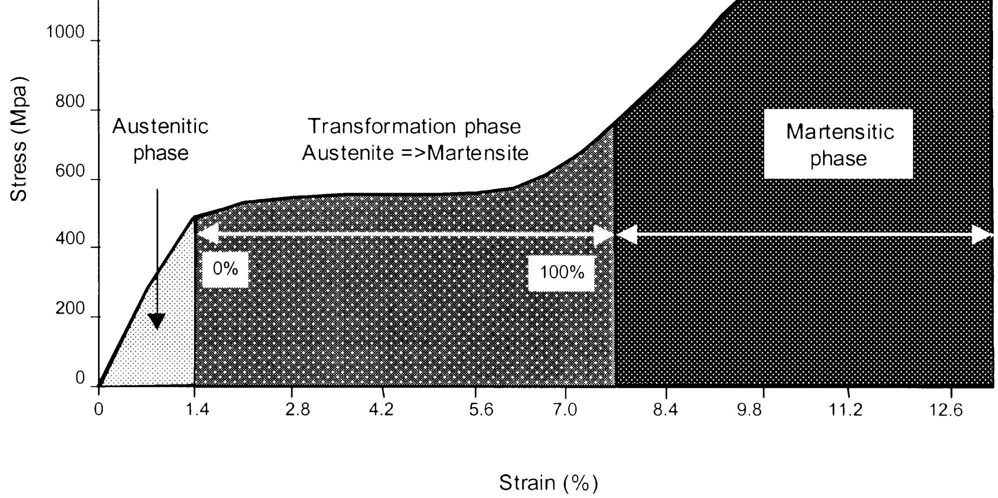

Figure 5 NiTi phase transformation.

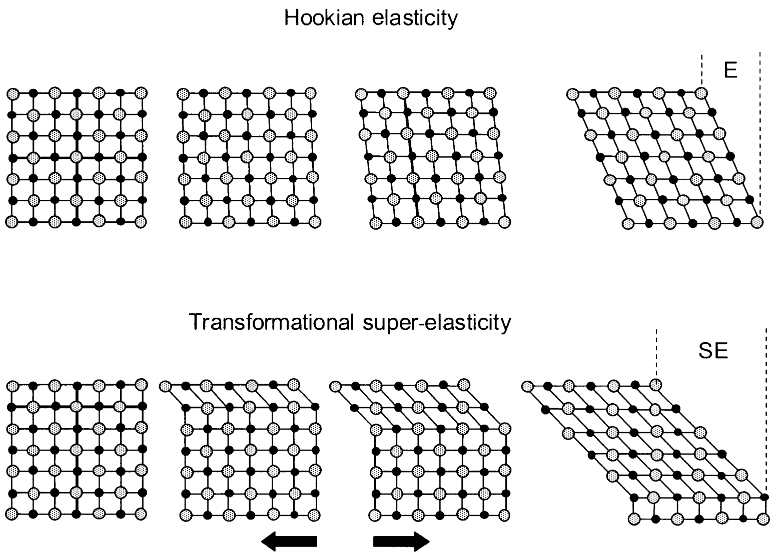

Figure 6 Diagrammatic representation of the tensile behaviour of stainless steel and NiTi super-elastic alloy and mechanisms of elastic deformation.

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).

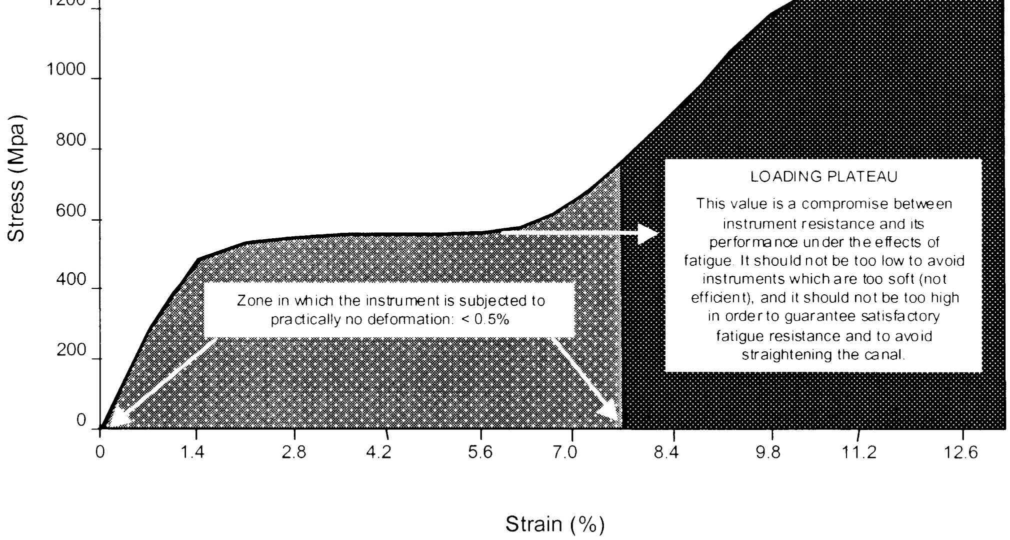

Figure 7 NiTi strength curve.

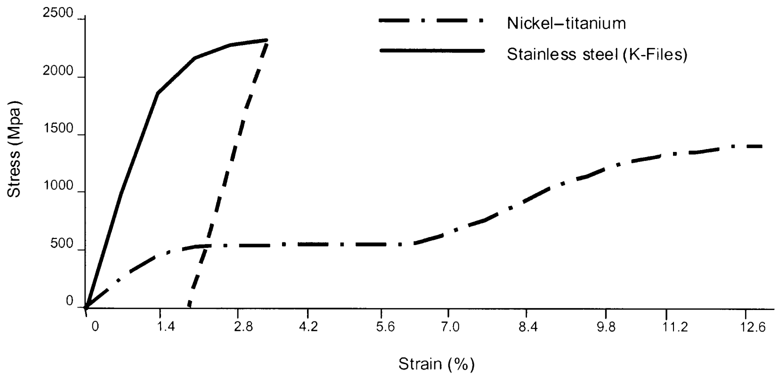

Figure 8 Stress-strain curve: stainless steel and nickel–titanium.

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.

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