SENTALLOY: The story of superelasticity

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Part I: History and basic concepts

Introduction
Since the days of Angle, many technological advances in archwires have enhanced our specialty, increased our efficiency, reduced our chair time, and as a result, increased our profitability. However, because of the great number of nickel-titanium alloys that actually exist, it is important to understand the historical background as well as basic concepts about them in order to visualize and recognize the clinical potential they have in orthodontics. Although nickel-titanium alloys appear to be the same, there are many small differences in their composition and manufacturing process, which inevitably make the difference between ordinary and extraordinary NiTi archwires.

The beginning of NITINOL
Nickel-titanium alloys have been found to be the most useful of all shape-memory alloys (SMAs): They are metals that demonstrate the ability to return to some previous shape or size when subjected to an appropriate thermal procedure. In other words they “remember” their original shapes. Other shape-memory alloys include copper-zinc-aluminum-nickel and copper-aluminum-nickel, but they do not possess the combined physical and mechanical properties of nickel-titanium alloys.

NiTi is unique because of the force levels expressed when heated, its corrosion resistance, its biocompatibility, the ease with which the TTR can be set and the reasonable cost of fabricating a precise alloy. A metallurgist, Dr. William J. Buehler, doing research at Naval Ordnance Laboratory (NOL) in White Oak, Md., discovered the unique shape memory properties of this alloy. NITINOL is an acronym used to describe a generic family of nickel-titanium alloys. It represents the two main elements of this alloy — nickel and titanium (NiTi) — and contains a reference to where it was developed in NOL, Naval Ordnance Laboratory.1

In 1958, Buehler was looking for a change in his professional career. An aerodynamics project at NOL was searching for the appropriate material for the re-entry nose cone of the SUBROC missile. Jerry Persh, the project manager, put Buehler to work assembling known property data on selected elemental metals and alloys that might be feasible.

Early in the developmental stages, secondary research on nickel-titanium alloys led to a significant application by Raychem Corporation. The produced a product called Cryofit, which was a hydraulic line coupler for the U.S. Navy’s F-14 aircraft. However, this was just the beginning of a wide range of new and exciting applications in medicine, dentistry and diverse engineering areas. Buehler retired from NOL in 1974 but remained involved in the development of NITINOL until 2005, at which time he moved to New Bern, N.C.

How NITINOL works
Exactly what made these metals “remember” their original shapes was in question after the discovery of the shape-memory effect. George Kaufman (Department of Chemistry of University of Fresno)
describes this process as follows: In a non-memory metal, the strain of deformation is absorbed by rearrangement of the crystals, and it is impossible to get the crystals back into the original position. On the other hand, in an alloy such as NITINOL the crystals stay in place: The atoms within the metal crystals rearrange themselves and the distorted objects revert to its original shape. There is no visible change in shape of the metal; all the changes occur at the atomic level.²

NITINOL had phase changes while still a solid; these phase changes are named martensite (low temperature) and austenite (higher temperature). The range of transition temperature (TTR) varies for different compositions from about -50°C to 166°C by varying the nickel titanium ratio or ternary alloy with small amounts of other metallic elements. Under the transition temperature, NITINOL is in the martensite phase. In the martensite phase, this alloy can be bent into various shapes; the crystal structure is disordered body-centered cubic. To fix the "parent shape" (austenite phase), the metal must be held in position and heated to about 500°C.

The high temperature "causes the atoms to arrange themselves into the most compact and regular pattern possible" resulting in a rigid cubic arrangement known as the austenite phase; the crystal structure becomes that of an "ordered" cubic, frequently called a cesium chloride (CsCl) structure. Above the transition temperature, NITINOL reverts from the martensite to the austenite phase, which changes it back into its parent shape.

NITINOL is a conglomeration of tiny regions of single crystals, called grains, all of random size, shape and orientation (Fig. 2). In the austenite phase the atoms of the grains adopt an atomic structure in which each nickel atom is surrounded by eight titanium atoms at the corners of the cube and each titanium atom is likewise surrounded by a cube of nickel atoms (Fig. 3). In the martensite phase, when the wire cools below its TTR, the grains change, which means that the nickel and titanium atoms assume a different and more complex three-dimensional arrangement (Fig. 4).

**NITINOL in orthodontics**

Another early application and probably the most important for the orthodontic world was the introduction of NITINOL into orthodontics as an archwire. In 1968, Dr. George F. Andreasen (Fig. 5) read
an account of a strange alloy discovered at the Naval Ordnance Laboratory (now the Naval Surface Weapons Center). He contacted Buehler, who sent Andreasen a number of different NITINOL composition in different processing conditions. Andreasen did extensive clinical research and found one of these alloys worked most effectively; he called this alloy the "memory wire" because it returned to its original shape after being bent. Andreasen’s 1978 article was the first to use the terms “shorter treatment times,” “less patient discomfort” (light forces) and “fewer archwire changes.” The wire was commercialized by Unitek Corporation and trademarked as NITINOL, identical in name to what Buehler had called it.

The first commercially available wire was 50/50 percent nickel to titanium and was a shape memory alloy in composition only. Cold working by more than 8 to 10 percent suppressed the shape memory effect. Nevertheless, what made it attractive compared to the competitive wires available at that time was its light force (about 1/5 to 1/6 the force per unit of deactivation), and its increased working range allowed it to be used in more severely maloccluded cases without taking a permanent set.

Andreasen reported his research on the thermal dynamic effects of NITINOL in the Angle Orthodontist in April 1985. Andreasen’s work on NITINOL earned him the 1980 Iowa Inventor of the year Award. He died in 1989 at the age of 55. This was the very beginning of nickel-titanium wires for orthodontics.

SENTALLOY: The first superelastic NiTi alloy
In the meantime in Japan, Dr. Fujio Miura (Fig. 6), who is the most famous orthodontic professor in Japan’s history, was making basic research on the biology of tooth movement with the objective to establish the "ideal concept of tooth movement." He was looking for a material or device that could deliver a constant and continuous force, and research was initiated to find a material that would satisfy this requirement.

In 1982, Miura and his university team made an offer to TOMY Incorporated (manufacturer of orthodontic products) and Furukawa Electric Co. (supplier of wire material) to do joint research on a new superelastic wire (Fig. 7). This new wire was characterized by its ability to generate optimal force for tooth movement and about 8 percent stress-induced martensitic transformation (superelasticity). This new NiTi alloy was launched in 1985 under the trade name of SENTALLOY (superelastic nickel-titanium alloy) (Fig. 8).

SENTALLOY had the features of superelasticity and shape memory. Miura describes these unique properties as follows.

**Shape memory**
Phenomenon occurring in an alloy that is soft and readily amenable to change in shape at low temperature but can easily be reformed to its original configuration when heated to a suitable transition temperature.

**Superelasticity**
A phenomenon that occurs when the stress value remains fairly constant up to a certain point of wire deformation. This is produced by stress, not by...
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Miura said that SENTALLOY allows a constant force to be delivered over an extended portion of the deactivation range and is therefore more likely to generate physiologic tooth movement and greater patient comfort. Using the body temperature to transform this alloy, SENTALLOY can address tooth movement resistance during an orthodontic treatment without causing trauma to surrounding dental tissues.

Miura believed that the discovery of the “superelastic” properties of SENTALLOY wires and its use in osteoclast recruitment was a significant scientific breakthrough for the orthodontic specialty. The use of superelastic wire established a new standard of biologic treatment in clinical orthodontics.6

**Part II: SENTALLOY historical overview**

For more than two decades, SENTALLOY archwire has found wide applicability in orthodontics and has developed products around the philosophy of applying physiological force for tooth movement.

- **1958,** Dr. William J. Buehler began experimental work on NITINOL at U.S. Naval Ordnance Laboratory (Fig. 1).
- **1976,** Dr. George Andreasen develops first NiTi alloy in orthodontics (Fig. 5).
- **1986,** Dr. Fujio Miura develops SENTALLOY the first Super-elastic nickel-titanium alloy (Fig. 6).
- **1987,** GAC International introduces the first superelastic open and close coil springs. (Fig. 9).
- **1988,** DERHT method for bending SENTALLOY wire was developing under the trade name of ARCH-MATE (Fig. 10).
- **1990,** NEOSENTALLOY appears, and it was the first time that was possible to use a full-size rectangular wire as initial wire that generates 100, 200 or 300 grams (Fig. 11).
- **1992,** BIOFORCE is introduced as the only superelastic wire that starts with low, gentle force for anterior and increases to the posteriors (Fig. 12).
- **1993,** GAC International creates Bioforce and NEOSENTALLOY IonGuard, a new nickel-titanium wire that underwent an ion implantation process (Fig. 13).
- **1993,** SENTALLOY MOLAR MOVER is created for molar distalization (Fig. 14).
- **1995,** TOMY Inc. introduces SENTALLOY STLH, a static termoactivity low-hysterisis, nickel-titanium wire (Fig. 15).
- **2000,** GAC PAKs enhances clean storage and dispensing of each wire (Fig. 16).
- **2008,** high esthetic archwires: SENTALLOY and Bioforce. Providing the same outstanding performance as standard wires, a rhodium process provides low reflectivity for reduced visibility (Fig. 17).

**Part III: Evaluation of mechanical and physical properties of SENTALLOY**

There are basically three types of laboratory tests — bending, tension and torsion — used to study the mechanical properties of orthodontic wires. Two more tests are used to evaluate physical properties:
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differential scanning calorimeter (DSC) and X-ray diffraction.

Although these tests do not necessarily reflect the clinical situations to which wires are usually subjected, they provide a basis for comparison of these wires with others NiTi wires. And in all of the tests, SENTALLOY has proved its efficiency as the only biologically correct archwire. Some of these examples are next.

A) Three-point bending test

In order to demonstrate the difference between the first NITINOL wire (3M Unitek) and the superelastic nickel-titanium alloy (SENTALLOY) in 1986, a three-point bending test was introduced by Miura. This test was designed to clarify the relationship between the loading and deflection by determining the nature of the force being delivered during orthodontic treatment. This method is acceptable to demonstrate the springback properties.

During cantilever bending, the wires of good springback property will increase the length and the angle of the specimens, so a superelastic-like property appears even if the wire does not possess this feature. Instead, a three-point bending test was designed because this would accurately differentiate the wires that do not possess superelastic features.

At the same time, the three-point bending test actually simulates the application of wire force on the teeth in the oral cavity. The deformation of NiTi alloys is induced with martensitic transformation; this can be reversed by heating the alloy to return to the austenite phase and is transformed by reversing back to the previous shape; this is produced by temperature.

Materials

Wire specimen of 0.016 round wires was selected: stainless-steel, Co-Cr-Ni, work-hardened and NiTi SENTALLOY. In order to simulate oral cavity environment the wires and the steel poles were set in a chamber at 37°C. The midpoint of the wire was deflected 2 mm at speed of 0.1 mm/min, under a pressure from a metal pole 5 mm in diameter (Figs. 18, 19).

Findings

Both stainless-steel and Co-Cr-Ni wires showed a linear relationship when the amount of deflection was 2 mm and the load was around 1300 g (Fig. 20).

As the deflection was removed, both of them showed a permanent deformation. NITINOL load deflection curve was almost linear; when the deflection of 2.0 mm was reached the load was 790 g (Fig. 21).

When SENTALLOY wire load-increasing ratio was 2.0 mm, the load was 650 g. However, when the deflection was decreased 1 mm from 1.6 to 0.6 mm, the load decreased by only a small amount, namely, values around 250–350 g (Fig. 22).

By evaluating the test results, SENTALLOY wire showed superelastic property and was physiologically compatible to the tooth movement because it provided continuous force for a long period of time during deactivation.

B) Tensile test

According to Miura, superelasticity can be produced by stress, not by temperature difference, and is called stress-induced martensitic transformation. Uniaxial tensile testing was performed all specimens were stretched using an Instrom universal testing machine.
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1. **UI: 12° Torque | U2: 10° Torque**: These values are optimal if full expression of torque is achieved. Thanks to the active clip, full expression can be achieved on a 0.019 x 0.025 ss wire. It is NOT necessary to increase/overcorrect these values.

2. **L1/L2: -5° Torque, 0° Tip, 0° Offset**: A small lingual crown torque overcorrection has been shown to help keep the incisors in an upright position when leveling and aligning and through Class II correction. 0° tip and offset makes all four incisor brackets interchangeable, facilitating bracket inventory.

3. **U3: 10° Tip**: This values has the optimal angulation. The increased mesial crown tip found in some prescriptions (13°) has shown undesired distal tip of the U3 root, frequently seen in x-rays. However, excessive uprighting (8° or less) could compromise proper coupling with the L3 and could also leave spaces in the upper arch that when closed, could prevent proper Class I relationship.

4. **L3: -8° Torque**: In many cases where the width of the maxillary and mandibular arches are normal, an excessive lingual crown torque (-11°), found in some prescriptions, makes proper coupling with the U3 difficult.

5. **U4/U5: -9° Torque, 0° Tip, 0° Offset**: Unique values are clinically insignificant, therefore the same values have been chosen, making them interchangeable providing bracket inventory flexibility.

6. **L4: 2° Tip | L5: -1° Tip**: Although this small difference of tip between the L4 and L5 will not be seen in non-extraction cases, it is significant in extraction cases to prevent “dumping” of the premolar into the extraction space.

7. **U6: -14° Torque | U7: -20° Torque**: Increased lingual crown torque, specifically for the second molar, facilitates the correction of the curve of Wilson and therefore arch coordination, while minimizing the use of auxiliaries such palatal bars, etc.

8. **L6: -25° Torque | L7: -20° Torque**: These values have been selected to facilitate uprighting L6/L7 preventing them from rolling lingually.

*Note: Values of torque, tip and offset refers to the crowns. Positive values of torque and tip mean buccal while negative mean lingual. Offset values are indicated as M (mesial) or D (distal).*
Case Study

14 year-old male with a blocked canine, end-on molar relationship and midlines off. In-Ovation ‘R’ appliance was used with extractions of maxillary first Premolar and mandibular second Premolar. Minimum anchorage mechanics was used.

Treatment time 20 months. • Case treated by Dr. Secchi

Initial intraoral photos showing maxillary right canine ectopically positioned, end-on molar and canine relationship and maxillary midline off to patient’s right side.

Intraoral photos at the time the In-Ovation ‘R’ appliance was placed with an upper and lower .014” Sentalloy archwires. Initial alignment was done in 7 months through a sequence of three archwires: .014” Sentalloy, .018” Sentalloy and .020” x .020” Bioforce.

After spaces have been closed, arches have been coordinated and proper overjet and overbite have been achieved, upper and lower .021” x .025” Braided finishing wires are used together with vertical triangular elastics for detailing and optimal occlusion.

Finished case. Proper intercusaption, Case I molar and canine with proper overjet and overbite. Minimum anchorage mechanics allowed maintaining maxillary and mandibular incisors inclination while protracting mandibular molars to a Class I relationship.
Materials
Wire specimens of 0.016 round wire stainless-steel, Co-Cr-Ni, work-hardened and NiTi SENTALLOY were selected; they were attached to a steel plate with epoxy resin at 37°C. In this figure, Y-axis represents the force generated by the wire and X-axis shows the strain that the specimens were stretched (Fig. 23).

Findings
For the stainless-steel and Co-Cr-Ni wires, the elastic modulus was 17–22 KG/mm²x103, showing very high values and a stress-strain curve to be almost straight during activation and deactivation phase. The elastic modulus of work-hardened NITINOL was 5–6 KG/mm²x103 and a stress-strain curve to be almost straight. Finally, in contrast, SENTALLOY showed a stress-strain curve of great significance that illustrates clearly the superelastic property.

When the wire was stretched it showed a straight curve. But when it reached 2 percent of its original length, it produced stresses of 55 to 58 Kg/mm² keeping those values until the strain was induced nearly to 10 percent (A to B). This diagram shows how the martensitic transformation begins at the 2 percent strain level and the transformation continues up to the 8 to 10 percent (Fig. 24).

When the martensitic transformation is complete, the whole specimen is transformed into the martensitic phase. When this occurs, the stress increases because of the elastic deformation. When the strain is removed (B to C), the stress decrease is linear because the elastic deformation occurs in the martensitic phase (Fig. 25).

Later, the martensitic transformation occurs again in the direction of the austenitic phase generating in a continuous force (C to D) (Fig. 28). In the final step, the martensitic transformation is completed and the wire is again in the austenitic phase (D to E). This elastic deformation occurs in the austenitic phase and the stress decrease is linear (Fig. 18).

The preceding metallurgical analysis indicates that SENTALLOY possesses superelastic properties (A to B range) and in the stress-strain curves (C to D range) (Fig. 19). The deformation of NiTi alloys and temperature changes induce martensitic transformations. These transformations are either stress (deformation) related or temperature related. Heating the alloy will induce the martensitic change (martensite to austenite) and removal of heat, cooling, (austenite to martensite) will return the wire to its original shape.

Bioforce
Miyazaki8 reported that a specific type of heat treatment (unlike the moderate temperature changes noted above) of SENTALLOY at 500°C would permanently and significantly alter the force plateau during unloading on a three-point bending test. This procedure created the possibility to manufacture SENTALLOY with three different levels of force. This same technology allowed a single wire size to have three different force levels. The optimal superelastic wire now offered light forces in the anterior section, medium force in the bicuspid area and a heavier force in the molar region.

In a three-point bending test, the superelastic properties of the wire become apparent in the molar region above a loading of 280 g (Fig. 29). At the premolar segment, the load/deflection curve reached a load of 180 g (Fig. 30). And the anterior segment the
wire demonstrated a superelastic plateau of 80 g (Fig. 31). It is possible to alter the superelastic characteristics of the wire in any desired section and apply an optimal force to each tooth with a single archwire.

This creates the possibility to obtain with a single archwire, the specific biological force to move specific teeth, with no patient trauma and fewer archwire changes (Fig. 32).

Bioforce IonGuard
To minimize friction, DENTSPLY GAC created a nickel-titanium wire that underwent an ion implantation process but did not affect the unique superelastic properties of Bioforce and NEOSENTALLOY. Ion implantation was originally developed for use in semiconductor applications. At low temperature, a high energy beam of ions are used to modify the surface structure and chemistry. The ion implantation is not a layer on the surface, therefore, it does not affect the dimensions or properties of the material and can be applied to virtually any material. Ion implantation improves wear resistance, surface hardness, resistance to chemical attack and, most importantly, reduces friction (Fig. 33).

Ryan9 showed that the ion-implantation process does reduce the frictional forces produced during tooth movement. This process tends to increase stress-fatigue, hardness and wear, regardless of the composition of the material.

The stainless-steel wire produced the least frictional force during in vitro tooth movement, followed by treated nickel-titanium, treated beta-titanium, untreated nickel-titanium and, finally, untreated beta-titanium. There were statistically significant differences in the amount of movement seen with the ion-implants wires compared with their untreated counterparts (Fig. 34).

Bedolla and Teramoto,10 in contrast with Ryan’s study, in an in vitro study reported that Bioforce IonGuard, which shows the smoothest surface (Fig. 35), generated the least frictional force, followed by stainless-steel and untreated NiTi, and the combination of Bioforce IonGuard with In-Ovation® brackets showed the less frictional forces (Figs. 36, 37).

Differential scanning calorimetry
Over the past decade, differential scanning calorimetry has been used to study nickel-titanium archwire alloys. In conventional DSC, two small pans, one containing the material to be analyzed and the other an inert reference material, such as indium are heated at the same rate, typically 5°C or 10°C per minute.

The changes in the thermal power difference for the two pans are related to changes in the heat capacity. It is useful for studying phase transformations in the nickel-titanium archwire alloys.

There are important phase transformations for nickel-titanium alloys: Temperatures at which the transformation from cooling begins, martensite-start (Ms); temperature at which martensite peaks or is finished (Mf or Mf); temperature at which austenite begins, austenite start (As); and temperature at which austenite peaks or is finished (Ap or Af).

In some cases, an intermediate R-phase (Rhombohedral crystal structure) may form during this transformation process.

Bradley et al.11 to clarify the differences in the phase transformation for major types of nickel-titanium wires, performed a DSC study, the results of which follow.
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Material
Wires tested: Four different Upper 016x022 NiTi archwires were tested — NITINOL-SE (3M UNITEK); Copper-NiTi 35 (ORMCO); NEOSENTALLOY F 80 (DENTSPLY GAC International); Bioforce-SENTALLOY (anterior section) (DENTSPLY GAC International)

Equipment
Differential scanning calorimeter (DSC) for measuring the austenite transformation temperature (Af point) was performed using a SII-DSC6220 Seiko Instrument (Fig. 39) and a thermal analyzer LN2 vessel was connected to DSC for cooling (Fig. 40).

Oral temperature
Sublingual temperature is routinely used as an indicator of oral temperature. It is approximately 37°C for most individuals, while not forgetting that many factors have been shown to affect the temperature in the oral cavity.

Temperature data should be considered during the manufacture and clinical use of temperature sensitive orthodontic materials like the nickel titanium wires. According to Moore12 if a single oral temperature were to be selected for the investigation of the in-vitro properties of orthodontic wires, 35.5°C would be more appropriate than 37°C.

Results
NITINOL SE
With NITINOL SE the complete transformation to austenite (Af) occurs at about 60°C, which is considerably above the temperature of the oral environment.

Copper NiTi 35
A single peak on the heating DSC curve, which corresponds to the martensite to austensite transformation indicates that the Af temperature (29.1°C) is under oral cavity temperature for copper NiTi 35.

NEOSENTALLOY
NEOSENTALLOY has a completely austenitic structure close to the temperature of the oral environment (32.7°C). There is also considerable hysteresis for the TTR in the forward and reverse directions for the complete transformation (martensite to austenite).

Bioforce (anterior section)
Just like NEOSENTALLOY, in the anterior section of Bioforce we see the complete transformation occurring very close to body temperature 32.5°C.

Summary
SENTALLOY archwires were the first reported superelastic nickel-titanium archwire in orthodontics. They are body heat activated and are capable of producing excellent treatment results because they deliver a light and constant force for a long period of time; which is considered physiologically desirable for tooth movement.

References