

Nickel-titanium alloys: A systematic review

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Objective: A systematic review on nickel-titanium wires was performed. The strategy was focused on Entrez-PubMed-OLDMEDLINE, Scopus and BioMed Central from 1963 to 2008.

Methods: Papers in English and French describing the behavior of these wires and laboratorial methods to identify crystalline transformation were considered. A total of 29 papers were selected.

Results: Nickel-titanium wires show exceptional features in terms of elasticity and shape memory effects. However, clinical applications request a deeper knowledge of these properties in order to allow the professional to use them in a rational manner. In addition, the necessary information regarding each alloy often does not correspond to the information given by the manufacturer. Many alloys called “superelastic” do not present this effect; they just behave as less stiff alloys, with a larger springback if compared to the stainless steel wires.

Conclusions: Laboratory tests are the only means to observe the real behavior of these materials, including temperature transition range (TTR) and applied tensions. However, it is also possible to determine in which TTR these alloys change the crystalline structure.

Keywords: Nickel-titanium wires. Thermoelasticity. Shape memory alloys. Superelasticity.

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INTRODUCTION

Metallic alloys that tend to return to the original shape after large deflections have been appreciated since the 50s. They have been studied not only for their use in Aeronautical Engineering, because of their sufficient ductility,²² but also in Medicine in the development of prostheses that replace long bones and in the study of surfaces and biofilms.¹⁴ In Orthodontics, these materials are used in archwires for the alignment of teeth, in the initial stages of treatment, when large deflection is necessary and also because they present a low modulus of elasticity (E) and excellent spring-back when compared to other alloys (Fig 1). Table 1 shows the nature of metallic alloys used in Orthodontics and their mechanical properties.

There is great variability in the amount of stored energy in same cross-section nickel-titanium alloys, available from different manufacturers. Many of them are commercialized as shape memory alloys, while others do not even show the effect of superelasticity¹⁷ and present characteristics of martensitic-stabilized alloys as the alloys originally known as Nitinol (Unitek, Monrovia, CA, USA). Some studies^{4,10,11,15,24} question the comparative methods by means of laboratory tests which do not correspond to the variability of clinical situations found.

The aim of this paper is to discuss the behavior of the mechanical properties of these alloys according to literature.

Characteristics and current status of nickel-titanium alloys

Nickel-titanium alloys were initially studied in laboratories by physicists in the beginning of the 60s⁸ and later developed for clinical use.¹ Due to the development of these alloys, new options have emerged such as the nickel-titanium arch wires with superelasticity and thermoelastic properties.

Initially, nickel-titanium wires presented greater flexibility when compared to other alloys, such as stainless steel, cobalt-chromium and titanium-molybdenum alloys (TMA). Nickel-titanium alloys, known by their brand name Nitinol (55% Ni; 45% Ti), are produced through industrial processes that characterize them by stabilized martensite, due to cold work.¹ Effectively, they do not

present the so-called shape memory effect or the superelasticity effect. They just present low modulus of elasticity (E) and large springback, in other words, wires made of these alloys are flexible and show linear behavior (Fig 2).

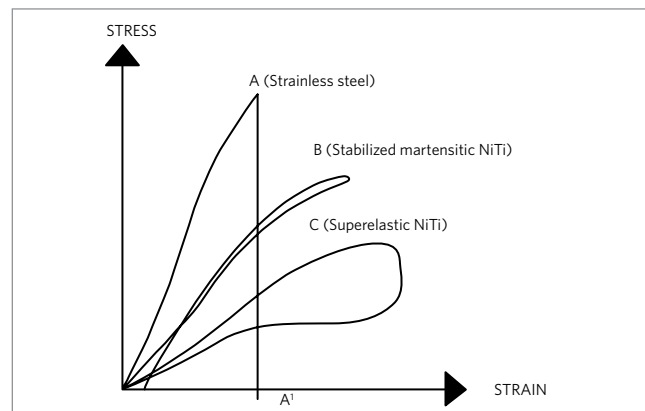


Figure 1 - Stress x Strain diagram. A, B and C wires present different stiffness. A represents stainless steel behavior; B represents stabilized martensitic wire (ex. nitinol) and C represents superelastic wire.

Table 1 - Wire material, Elastic limit (σ_e) and Elasticity modulus (E).

Wire material	Elastic limit (MPa)	Elasticity modulus (E) (GPa)
Stainless steel	1720/1543-1966	193
Titanium molybdenum	1240 1380/769-1254	65-100
Cobalt-chromium	1792	193
Nickel-titanium	1650	33

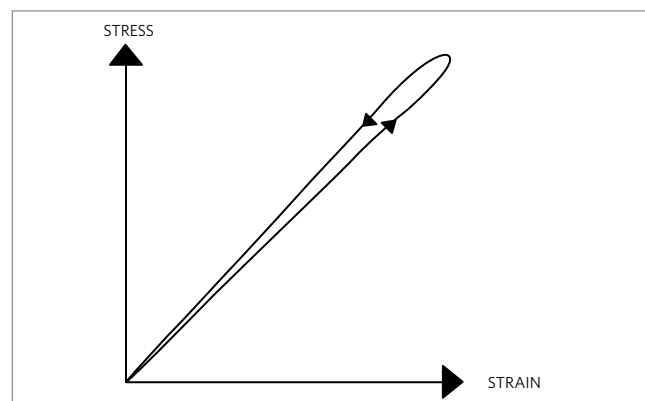


Figure 2 - Stress x strain graph. Analyzing the graph, this could be a martensitic alloy-stabilized, as well as a superelastic alloy, the deformation of which was not sufficient to cause the effect of superelasticity (plateaus). There are superelastic alloys whose A_f is so low that it is useless for clinical use because does not suffer crystal change with the forces commonly used in the daily clinic.

Nowadays, nickel-titanium alloys known as martensitic-stabilized (Nitinol), austenitic active and martensitic active alloys^{10,26} are available. Austenitic active and martensitic active alloys present different rigidity depending on temperature and as show the thermoelastic effect or shape memory. For the martensitic-stabilized alloys, it is expected only good elasticity effect, thus having good springback; however, they can be deformed permanently, if a certain limit is exceeded or due to long time remaining in the mouth (moderate or severe crowding, for example). Superelasticity or shape memory effects should not be expected. Austenitic active alloys should present the effect of superelasticity (also known as pseudoelasticity,²⁶ confirmed by curve with plateaus, which are not possible in martensitic-stabilized alloys). Many NiTi alloys are described as binary, in other words, they are characterized as presenting two phases, one NiTi matrix phase and a precipitation phase Ni₃Ti₄.¹²

Martensitic alloys are characterized as ductile and plastically deformable, while austenitic alloys are stiffer and not plastically deformable³. In a more simplistic way, it might be stated that austenitic active wires are more flexible and have good springback at room temperature; and if a certain tension (force) is applied upon them, small areas of martensitic crystalline structure might be formed, making them less stiff in these areas and, consequently, easier to fit in a slot. In other words, little islands of crystalline martensitic structure are formed in a predominantly austenitic body. On the other hand, martensitic active wires show, at room temperature, very poor resistance to stress and discrete springback, so that they seem to accept a certain bend and, after removing it, the wire moves discretely toward the original shape, but without success because of the force decay. However, as they receive heat from the mouth, they initiate an austenitic crystalline alteration, becoming more resistant to stress and regaining their initial shape, confirming the shape memory effect. Once the heat is removed or the wire is cooled down, they present their initial characteristic, having predominantly a martensitic crystalline structure. In this alloy exist a mixed or rhombohedral phase "R" at room temperature that coexist with austenite and martensite structure.

MATERIAL AND METHODS

Articles related to the topic were researched (Entrepreneur-PubMed – U.S. National Library of Medicine e BioMed Central) from 1963 to 2008. The words NiTi wires were accessed and 375 occurrences were found. Among these occurrences, we have selected articles that contained information about tension tests, torsion tests, bending tests or other methods for verifying the behavior and crystallography of nickel-titanium alloys. A textbook on Biomedical Engineering was also used as source of information.

DISCUSSION

In graphic terms, the crystalline transformation of the austenitic active nickel-titanium alloys might be demonstrated by a straight line with a certain inclination, indicative of its degree of rigidity (E), which after a certain magnitude of applied bend, goes through a crystalline transformation (molecular arrangement), changing from austenite to martensite, represented by plateau A (Fig 3), indicating that regardless of more wire deformation, the tension is practically the same. In other words, the tension is constant along the resulting deformation. After the tension is removed (for each tension applied there is a corresponding force), the curve shows a decrease at its tension magnitude, with a new inclination and, consequently, new rigidity, until a new plateau B is formed, though at a smaller tension magnitude.

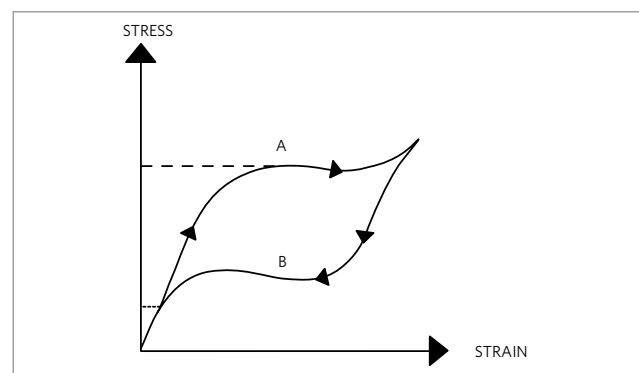


Figure 3 - Stress x strain graph. Typical curve for a superelastic alloy, forming plateaus. The plateau A represents the crystalline martensitic change at a certain level of tension, while plateau B represents a new martensitic transformation, but at a lower voltage level. Between A and B there is new formation of austenite with stiffness equal to that prior to the plateau A. The plateau A is formed due to the stress-induced martensite, due to metal arc be attached to the slot brackets, while the plateau B is formed due to the reduction of tension (motion toward the dental arch alignment).

The difference between the plateaus is explained by the phenomenon of hysteresis (loss of energy because of crystalline alteration). After the tension is removed, reverse crystalline transformation from martensite to austenite occurs. This graph describes the superelasticity effect, not observed regarding the martensitic-stabilized alloys, such as Nitinol.

The effect of superelasticity introduces a new property of metallic alloys, characterized by the appearance of martensitic crystalline structures in an austenitic structure, after the use of a certain stress. This generates areas of stress-induced martensite (SIM) which takes place in the parts of the metallic wire tied to the brackets of the most unaligned teeth; however, as the teeth get aligned, these areas of induced martensite disappear and are replaced by austenite, since the induced martensite areas are very unstable. Depending on the manufacturer, the nickel-titanium wires have a temperature range in which it is possible to observe the effects of crystalline alteration. This range of temperature is known as transition temperature range (TTR) and it presents final and initial limits, denominated – for the austenitic crystalline structure – as final austenite (Af) and initial austenite (As); thus, in Af temperature the maximum elasticity of these alloys takes place, while in As temperature weak elasticity is observed. For the martensitic active alloys there is also a temperature range in which these phenomena take place; thus, Mf and Ms indicate a higher level of martensite and lower level of martensite, respectively. Many of these wires are sensitive to applied tension and to temperature. Focus is on the concept of crystalline TTR, the temperature range in which some crystalline transformation might take place, and the austenitic final temperature was defined (Af), in which the alloy reveals a high stiffness phase, as well as the final martensitic temperature (Mf), in which the alloy reveals a low stiffness phase.

Figure 4 shows the characteristic curve of shape memory for the wires, Ms and Mf represent the temperatures where crystallographic martensitic alteration begins and where it ends, respectively. On the other hand, As and Af temperatures represent where the austenitic alteration begins and

ends, respectively. Therefore, there is martensitic transformation between Ms and Mf temperatures and the wire might present characteristics of plasticity; on the way to As temperature, the wire begins to show greater rigidity. It might be stated that superelastic wires may return to the initial shape when a force is abruptly applied and when a force of considerable magnitude is removed. In the martensitic stage, two effects are noticed: In the first one, after some initial deformation, the crystallographic variants that might be found in 24 shapes of coexisting martensite and after the removal of force, these variants reorganize themselves in their initial positions and the wire returns to its original shape. In the second case, the nickel-titanium wire shaped in the austenitic state is cooled down until it reaches the martensitic state. If during the process the material is deformed, it returns to its initial shape after heating and this phenomenon is called shape memory effect.¹⁶ Austenitic structures are face-centred cubic α phase while martensitic structures correspond to body-centred cubic β phase. They have exactly the same chemical constitution, but because of their different crystallographic structure, they do not exhibit the same mechanical behavior.² Between iM and fA there are initial levels of each transformation where the alloys begin to show some crystalline transformation. The highest temperature in which it is still possible to find the formation of martensite is called Md.¹⁹

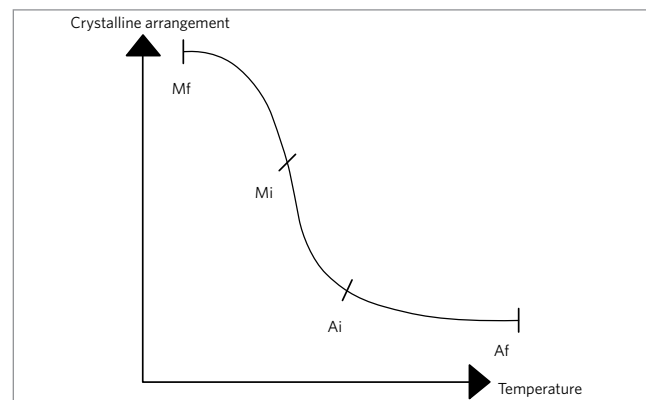


Figure 4 - Austenitic-martensitic transformation of crystalline arrangement vs. temperature.

Table 2 - Reviewed literature, authors, wire material and applied tests.

Authors	NiTi nature	Test / Method
Nakano et al ²⁴	Superelastic NiTi wires with different cross-sections	Three point bending test
Augereau et al ²	Shape memory NiTi (Cu-Zn-Al)	Echography and acoustic microscopy
Parvizi, Rock ²⁵	Supereleastic NiTi 0.40 mm and 0.40 x 0.56 mm	Three point bending tests (20°C, 30°C and 40°C)
Santoro, Beshers ²⁷	Thermoelastic and superelastic NiTi wires 0.017 x 0.025-in	Three point bending tests
Buehler, Gilfrich, Wiley ⁸	NiTi wires	X-ray diffraction (XRD), tension tests, compression tests
Andreasen, Hilleman ¹	NiTi Wires - stoichiometric composition	X-ray diffraction, tension tests, compression tests
Uchil ²⁸	Nitinol cold-worked 40% wire sections of 6 cm	Dilatometric measurements and electrical resistivity
Burstone, Quin, Norton ⁹	Chinese NiTi (superelastic) 0.016-in	Torsion tests
Miura et al ²¹	Japanese NiTi (superelastic)	Three point bending tests
Gurgel et al ¹⁵	Superelastic NiTi wires 0.017 x 0.025-in	Torsion tests
Filleul, Constant ¹¹	NiTi (superelastic) 0.017 x 0.025-in	Torsion tests and differential scanning calorimetry (DSC)
Bradley ⁵	NiTi wires (superelastic)	Differential scanning calorimetry (DSC)
Brantley et al ⁶	NiTi wires (0.016-in, 0.016 x 0.022-in and 0.018-in) superelastic and shape memory	Differential scanning calorimetry (DSC)
Brantley et al ⁷	Copper NiTi (35°C), 0.016 x 0.022-in	Differential scanning calorimetry (DSC) and temperature modulated differential scanning calorimetry (TMDSC)
Iijima et al ¹⁷	Copper NiTi (35°C), Neo-Sentalloy and Nitinol SE 0.016 X 0.022-in	Torsion tests X-ray diffraction (XRD)
Filleul, Bourgoïn ¹⁰	SS, CoCr, NiCr, Titanium-molybdenum and Nitinol wires	Torsion tests
Fischer-Brandies ¹²	Superelastic NiTi wires: 0.016 x 0.022-in, 0.017 x 0.025-in, 0.018 x 0.025-in	Bending tests (22°C, 37°C and 60°C)
Meling, Ødegaard ¹⁸	Superelastic NiTi wires, Nitinol and titanium-molibdenum wires: 0.016 x 0.022-in, 0.017 x 0.025-in and 0.018 x 0.025-in	Torsion tests (25° torsion angle at 37°C)
Meling, Ødegaard ¹⁹	Superelastic NiTi wires (0.017 x 0.025-in and 0.018 x 0.025-in)	Torsion tests (25° torsion angle) at 18°C, 27°C, 37°C and 40°C
Meling, Ødegaard ²⁰	Superelastic NiTi wires (0.018 x 0.025-in) and thermoelastic wires (Copper NiTi 0.017 x 0.025-in)	Torsion tests at 20° (10°C to 80°C)
Barwart et al ⁴	NiTi Japanese coils (50 g, 100 g, 150 g and 200 g)	Differential scanning calorimetry (DSC)
Somsen et al ³⁰	NiTi (51% < x < 54%)	Thermal control, electrical resistivity, X-ray diffraction
Bartzela et al ³	Thermoelastic NiTi wires 0.016-in, 0.016 x 0.022-in, 0.017 x 0.025-in and 0.018 x 0.025-in	Three point bending tests
Garrek, Jordan ¹³	Superelastic NiTi wires (0.016 x 0.016-in, 0.018 x 0.018-in and 0.020 x 0.020-in)	Three point bending tests at 37°C ± 5°C
Schneevoigt et al ²⁹	NiTi coils (different geometries)	Compression tests (27°C, 37°C and 47°C) Applied (0,5 N to 3,5 N)
Muraviev et al ²³	Superelastic NiTi wires (0.014-in, 0.016-in, 0.018-in and 0.020-in)	Mathematical model (large deflections)

Martensite normally forms at the M_s (martensite start) temperature but can form prematurely above the M_s temperature if stress is present. Below the M_s temperature, deformation occurs by martensitic twinning. Between the M_s temperature and the austenite final A_f temperature, the martensite is stress-induced but once induced is stable.¹⁹ Above the M_d temperature, the deformation is due to slip, because martensite can no longer be stress induced.¹⁹ Table 2 shows the variety of studies developed according to the type of test.

To the effect of crystalline transition within a certain temperature range take place at A_f temperature (final austenitic), representing the highest level of occurrence of this crystalline structure, the alloy should be manufactured to respond with good springback for a temperature lower than that of the mouth (e.g. around 27°C), but if it is manufactured to have an A_f of, for instance, 10°C, the alloy will be predominantly austenitic at 10°C; thus, if exposed to a 37°C temperature, the wire would not be useful, considering that the 37°C – 10°C range is large and the wire would be too stiff working as a stiff elastic wire, without presenting the effect of superelasticity or, in other words, pseudoelasticity. Moreover, greater stress would be necessary to induce or keep stress induced martensite (SIM) for a longer period in order to produce a prolonged dental movement. It because there is a greater chance to find austenite in the temperature mentioned in the example given. In addition, stress induced martensite (SIM) is highly unstable. However, if produced to have an A_f of 27°C, the gradient would be 37°C – 27°C, therefore, islands of unstable martensite would be present and the wire would show superelasticity.²⁵ Concerning a wire produced for an A_f of 35°C, the gradient would be so small that this wire would be recommended for use in adults, because the level of austenite would be weak, or in other words, austenite and martensite stages would coexist. In addition, there is evidence that SIM may alter the crystalline transformation temperature towards higher temperatures, making the return to an austenitic crystalline structure difficult.^{16,27} The temperature gradient will, therefore, modulate the crystalline transformation. Thus, if we confront an arch with a certain A_f temperature, the difference between

the temperature specified for the arch and the temperature of the buccal cavity is the gradient, and it will determine the degree of transformation.^{26,27} In this way, the arches available as thermoelastic, with TTR (A_f) 40°C, will be less austenitic in their crystalline structure than those with TTR (A_f) 27°C, due to a higher gradient in relation to the temperature of the buccal cavity (37°C), as exemplified. Arches with higher crystalline TTR have been provided to be used in patients who had a history of periodontal problems because the arches would effectively act only when the patient eat some hot food.

It is necessary to know if the discussed arch presents enough resilience to take the springback to the expected torsional moment during unloading, that is to say, if this arch presents the second plateau at force levels that are not so low, preferably close to the first plateau, meaning lower hysteresis. In other words, it would be important to have an arch that allowed us to obtain martensitic transformation with little stress, and later, due to buccal temperature, the arch would go through austenitic transformation, and that would help the unloading of the torsional moment to take place in a more profitable way, but without much hysteresis (loss of energy due to crystalline alteration). Arches with “higher temperature” will not be effective for the effect of torsional moment; consequently, it would be preferable to choose arches with crystalline TTR from 22°C to 27°C. Stress might interfere upon the mechanical properties of the alloy, as well as upon the TTR, i.e., it might increase the A_f of an alloy, or decrease it. Resistivity tests²⁷ show that the curve of resistivity gets flatter, indicating that crystalline alteration decreases from one stage to another. The more an elastic alloy is bent to fit in the slot, more A_f is increased, consequently a higher temperature will be necessary for superelasticity to take place; higher temperature will be necessary to undo the martensite islands formed during the bending of the wire, and for the alloy to guide the tooth to the end of the elastic work of the arch, meaning that a higher temperature will be needed for the conversion of martensite into austenite (the alloy cannot regain its austenitic stage).

Studies⁴ about the TTR of nickel-titanium Japanese NiTi closed coil springs (Sentalloy, GAC

International, Bohemia, USA), with different force magnitudes (50 g, 100 g, 150 g and 200 g) using differential scanning calorimetry technique (DSC) have concluded that the springs became superelastic when the temperature increased and would no longer be superelastic when the temperature decreased at M_f . Both M_f and A_s temperatures were below buccal temperature. At room temperature and some degrees below the tested springs showed the superelasticity effect, and that would fit the purposes of orthodontic use, even when considering the alterations of buccal cavity temperature, such as during meals. In this way, for the superelasticity effect to become useful in orthodontics, the transitional crystalline alterations (martensitic-austenitic or austenitic-martensitic), must take place at temperature a little below the mouth temperature.

Sentalloy alloys present a transitional temperature that varies from 8°C (A_s) to 28°C (A_f) at maximum stress, but when buccal temperature is 36°C or 37°C , they just show the austenitic stage, unless the temperature drops below 28°C . On the other hand, Copper NiTi 35°C alloys (Ormco, Orange, CA, USA) are superelastic at 35°C (A_f) and only below 7°C (A_s) turn to martensitic; however, with induced stress, the TTR stands between 23°C (A_s) and 41°C (A_f); consequently, when the temperature is below 23°C , only the conventional elastic effect takes place, making the alloy return force not meaningful²⁷. Figure 5A shows a clinical situation where the nickel-titanium arch does not allow total

contact with the bracket slot, meaning that the plateau could not be reached; consequently, it would not be working as superelastic, or it was not possible with such stress to produce crystalline alteration with the formation of martensite in that wire. On the other hand, in situation B (Fig 5B), the arch could fit the slot completely, presumably reaching the plateau, once this wire allowed the crystalline martensitic transformation to take place with the same stress. If the wire is forced into the bracket, as in situation A, stress induced martensite is being produced at a very high force level, which not only is not interesting for clinical application, but also might plastically deform the wire, and consequently the mechanical properties of the alloy, the TTR change and the correspondence between this temperature and the buccal temperature range is lost. Thus, a stage of transformation of austenite into martensite, or vice versa, might be altered and the alloy will not express its characteristics and will behave only as a resilient alloy, elastic with a lower elasticity model. In this way, a clinician might purchase an expensive alloy, without effectively using properties. The alloy will not be able to move the tooth effectively, in other words, the alloy will not reach its final transition temperature (A_f) because it was poorly chosen for that clinical situation.

Since the first studies⁸ about nickel-titanium alloys were introduced, the alloy have improved in mechanical properties in order to respond to clinical needs, but laboratory studies have shown that

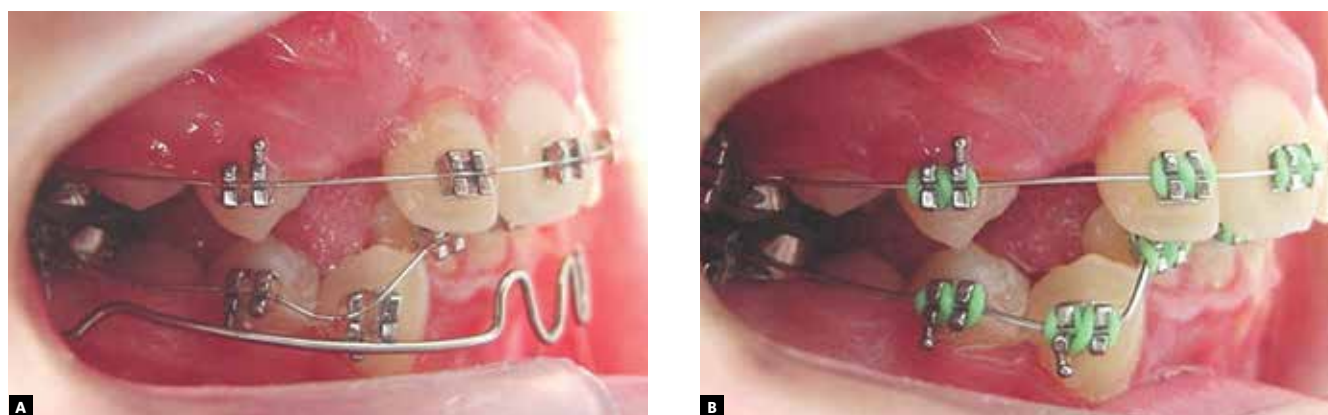


Figure 5 - A) Clinical situation where is not possible to insert a NiTi wire into the bracket slot. This situation can occur when superelastic wires can not reach a plateau, i.e. impossible to produce SIM in clinical levels. **B)** In this situation SIM formed and the wire could be fitted into the slot bracket.

there is a lack of characterization of these products. Manufacturers commonly do not specify the real characteristic of the arches.

A lack of reproducibility of the description of properties has been observed. Therefore, many arches available as superelastic do not behave as, others show a very high TTR in which there is crystalline alteration, from the stage where the alloy is totally martensitic until the stage where it is totally austenitic, so that they do not reveal a meaningful effect in the buccal cavity. That happens due to the little difference in temperature between the buccal cavity and the final austenitic temperature of the alloy (temperature gradient) or due to the fact that the wires commercialized present transition temperatures calculated for unstressed situations, consequently not simulating several stress applied situations, such as constant stress conditions in cases of misalignment because of lack of space.

Studies¹¹ have shown that at higher the temperature, more difficult it will be for the arches to reach stress induced martensite through applied tension. There are arches whose transition temperature is negative; thus, even before being placed in the mouth, they already show a certain rigidity, so it will be more difficult to insert them totally in the bracket slot, that is, the arches do not reach the martensitic structure, do not form a plateau and an absurd amount of tension would be required, clinically not common, to produce SIM. Arches with such behavior cannot be called superelastic (Fig 1).

Researches developed through the calorimetry technique, by means of temperature modulated differential scanning (MDS), have shown that the stages of transformation of Copper 35°C NiTi alloys (Ormco, Orange, CA-USA) require an intermediate R stage; besides, oxide precipitate and density differences are due to the reaction of nickel-titanium with residual oxygen found in the environment.⁶

The literature shows that the classification and understanding of the properties of these alloys become confusing due to the complexity of these phenomena and only studies based on research are capable of determining real effects. Commercially, these alloys are described in a very simplistic way considering their advantages. Researches show that these materials present complex behavior and

cannot be examined in an isolated manner.

The first alloy used in Orthodontics, known commercially as Nitinol, did not have the effects of superelasticity, only a discrete shape memory effect, with low rigidity, due to its manufacturing process which produced an alloy with mechanical hardening characteristics (cold work machining that increases the size of grains, altering then the mechanical properties of the material). That is verified by the fact that after removing the arch, after a certain period of use, it was plastically deformed (martensite-stabilized in a passive way), if alignment was more severe, these alloys were characterized as being martensite-stabilized and had a very discrete shape memory effect, with temperature increase.

The metallic alloys, in general, might also be studied by examining metal phase transformation diagrams, which reveal the microstructure of the alloys and, as a result, how they will behave concerning their physical properties. Other methods, such as X-rays diffraction (XRD), which allows the study of several crystallographic forms of nickel-titanium³¹ alloys, the differential scanning calorimetry (DSC)^{5,6} technique and the most recent known as temperature modulated differential scanning calorimetry (TMDSC), are effective means to access the stage transformations that are generated after applying tension or torsion upon these alloys; however, diffraction by X-ray reveals itself as more limited for penetrating less than 50%.⁷

Research¹⁷ using nickel-titanium alloys by means of X-ray diffraction (XRD), with transformation stages at low temperature varying from -110°C to 25°C, was compared to the results of previous studies⁷ performed using the TMDSC technique. For the study, alloys commercially known as Copper NiTi 35°C (Ormco, Orange, CA, USA), Neo Sentalloy (Sentalloy, GAC International, Bohemia, USA) and Nitinol SE (3M Unitek, Monrovia, CA, USA) with transversal section of 0.016 x 0.022-in were selected. All the samples studied were superelastic, although the Neo Sentalloy (GAC International), samples are commercialized as having shape memory. A more complete study should take into consideration the complementarity of techniques such as XRD, TMDSC and TEM (transmission electronic microscopy). X-ray diffraction

(XRD) shows peaks characteristic of the martensitic transformation technique. Thus, non-superelastic alloys are austenitic at room temperature, and that denotes that the martensitic stage is found at very low temperatures.⁷

A study² was performed with shape memory alloys (Cu-Zn-Al) by means of echography and acoustic microscopy in order to observe the crystalline changes in the grain structures step by step. The structures of these alloys (38,5% Zn face crystalline transformation at temperature close to room temperature) have the same chemical constitution, but different crystallographic structure. Martensitic and austenitic structures are cubic of centered body (phase β) and cubic of centered face (phase α), respectively, and that explains the fact that they do not show the same mechanical behavior. Martensitic structures reveal themselves to be as straight slip bands inside the austenite grains, while austenitic structures show grains with different shades of gray.

A study²⁸ performed by means of DSC and electrical resistivity to crystalline transformation in two stages, NiTi and NiTiCu (300°C to 800°C) alloys, found that the R stage is suppressed in NiTi-Cu alloys due to the addition of copper, while NiTi alloys present this intermediate stage from 340°C to 410°C; however, above 410°C there was no production of R stage.

The effect of superelasticity was observed in nickel-titanium arches through tension (axial) and stress tests.²¹ Nickel-titanium arches (Chinese NiTi, GAC International, Bohemia, USA) tested by means of stress tests to determine the rigidity, springback and the maximum force of stress, for large activations, showed rigidity of about 7% compared to the one found in stainless steel, while in activations of little amplitude, rigidity was 28% in relation to stainless steel. These alloys showed excellent springback capacity, and they might be stressed 1.6 times more than nickel-titanium Nitinol SE (3M, Unitek, Monrovia, CA, USA) alloys. They show a transition temperature a little below mouth temperature, but they are austenitic in this temperature, so they do not reveal effectively the thermoelastic effect, while allowing the production of stress induced martensite.

In three point stress tests with 42 samples of

NiTi alloys of 0.016-in and 0.016 x 0.022-in, which were produced by 9 different manufacturers, we noticed that there was a difference among the samples concerning the stored load with the same transversal section.²⁴

The behavior of crystalline transformations, and chemical and topographical compositions of the surfaces of NiTi alloys of different commercial brands, in the shape of rectangular wires (0.016 x 0.022-in.) such as Neo Sentalloy F80 (Sentalloy, GAC International, Bohemia, USA), Thermo-Active Copper NiTi (A-Company, San Diego, CA, USA; Ormco, Orange, CA, USA), Rematitan LITE (Rematitan 'Lite' nickel titanium, Dentauro, Germany), Titanol SE S (Forestadent Bernhard Förster GmbH, Germany) and Titanal (Lancer Orthodontics Corporation, USA), showed that besides the austenitic and martensitic stages there is a stage called R phase. The tests were performed within different temperatures (22°C, 37°C and 60°C). The chemical composition and surface analysis tests were performed by means of X-ray spectroscopy, through a scanner attached to an electronic microscope. Regarding the different temperatures analyzed, differential scanning calorimetry (DSC) was used, varying from -80°C to +80°C. The mechanical properties were analyzed through three point stress tests. The stress tests showed plateaus during the loading and unloading of tensions.¹²

In recent research^{19,20} the rigidity of nickel-titanium wires during activation and deactivation was observed. It was concluded that if a superelastic alloy is submitted to cold water during its activation phase, the stress force drops and remains at a sub-baseline level until it is once again heated (transient effect). On the other hand, if the alloy is rapidly cooled, during deactivation, the force drops temporarily and the sudden heating induces a transitory increase in the rigidity of the alloy during activation, but with prolonged effect, when heated, during springback (deactivation). The higher the degree of activation (tension) used for activation (dislocation), more springback will become possible during the deactivation phase. The amount of stress required to induce the production of martensite increases as temperature increases from Ms (initial martensite) to Md temperature (maximum

temperature where martensite might still be found), in other words, the higher is the tension (stress) applied, the higher the temperature, so that austenitic transformation becomes possible.²⁰

Three point stress tests with NiTi thermoelastic alloys have shown great variability, qualitative and quantitative, performance, since many alloys have remained deformed after the test, and others showed weak or no superelasticity. A study³ that involved 48 thermoelastic alloys of transversal sections 0.016-in, 0.016 x 0.022-in, 0.017 x 0.025-in and 0.018 x 0.025-in classified them as true superelastic when the plateau showed deflection $\geq 0,5$ mm; superelastic borderline when the plateau showed deflection $< 0,5$ mm and $> 0,05$ mm and non-superelastic when the plateau showed deflection $\leq 0,05$ mm.

The rigidity effect of nickel-titanium alloys was studied concerning the transversal section. Thus, superelastic alloys were used (Ortho-Force, France) with square transversal sections (0.016 x 0.016-in, 0.018 x 0.018-in, and 0.020 x 0.020-in). The Modulus of Elasticity (E) seems to vary according to the transversal section, but it depends on the amount of martensitic transformation which took place during the phase transformation. An alloy of larger transversal section will not necessarily produce higher forces, meaning that rigidity during stress is not directly related to the transversal section when the superelasticity process takes place.¹³

Torsion tests using superelastic and thermoelastic alloys, aiming to understand the behavior of alloys under thermal variations and according to different degrees of torsion, have shown that the alloys could not respond to temperature variation and remain at a sub-threshold level when there was a change from a high to a low temperature and then back to a high temperature. They could not regain their resistance to torsion. In some tests (temperature varying from 10°C to 80°C) there was a simulation of the thermal changes that take place in the buccal cavity after the ingestion of food. In other torsion tests (25°) superelastic alloys at 18°C, 27°C, 37°C and 40°C did not show martensitic change, but showed plateaus only in 45° and 60° torsions, which would not produce torsion on incisors, since the advocated torsion ranges from 7° to 22°.¹⁸

In another study¹⁹ involving NiTi superelastic

alloys compared to conventional ones and to β -titanium alloys 0.016 x 0.022-in, 0.017 x 0.025-in and 0.018 x 0.025-in sections and 25° torsion at 37°C, it was found a variation in torsion resistance among different alloys and among different manufacturers, and only one alloy tended to superelasticity.

The effect of torsion upon metallic wires of 0.017 x 0.025-in and 0.018 x 0.025-in transversal sections of different types of alloys commonly used in orthodontics, was studied by means of a device that simulated a dental arch. The wires were inserted in the brackets of a patient simulator. At 15° activation, Tru-Chrome Stainless Steel 0.017 x 0.025-in wires (RMO, Denver, CO, USA) restored a torsion 4 times stronger than that of a Nitinol SE 0.017 x 0.025-in wire (3M Unitek, Monrovia, CA, USA).¹⁰

Torsion effects have also been examined in laboratory tests aiming evaluate the rigidity of nickel-titanium alloys. Torsion tests have shown that some samples presented curves without plateaus, and that represents lower energy stored due to differences between martensitic transformation temperatures and those simulating buccal cavity¹⁵ temperatures.

Copper enriched nickel-titanium alloys have shown a decrease in their rigidity and hysteresis, and that would produce a lower moment necessary for activation. However, during deactivation, these alloys could not totally produce the necessary torsion. This paper has demonstrated that in order to select an appropriate superelastic alloy, consideration should be taken not only in the transition temperature, but also rigidity; nevertheless, there is variation between rigidity levels, according to manufacturers and some alloys reveal torsion moments comparable to those of conventional nickel-titanium alloys.

Torsion tests have shown that orthodontic wires whose martensitic phase begins at very low (negative) temperatures depend on a higher unloading torsional moment to form the plateau. In this way, these plateaus would never be reached and, consequently, the wire would behave as a stainless steel wire and the only advantage would be showing a lower modulus of elasticity (E); however, the wire would not reveal any characteristic of superelasticity (formation of plateaus). It has been noticed that the superelasticity effect is influenced by the chemical composition of the nickel-titanium wire (e.g. Ni

content) as well as by room temperature; thus, if Ni content is higher, there will be a decrease in temperature for initial martensitic transformation, and a higher force moment would be necessary to induce martensite, meaning that martensite already begins at low temperatures. As a result, at a higher room temperature, there would already be austenitic transformation and greater applied tension would be necessary to produce SIM transformation.¹¹

Somsen et al³⁰ studied the effect of thermal treatment on the formation of R phase, in Ni-rich NiTi alloys, which is related to Ni_4Ti_3 precipitates. The effect of electrical resistance in NiTi (51% < x < 54.5%) alloys, $\text{Ni}_x\text{Ti}_{x-100}$, cooled at several temperatures (T_A) and at room temperature, was studied and it was noticed that when the alloys were cooled, at a B2 phase ($T_A=1273\text{K}$) of alloys with 51% < Ti < 54%, there was an increase in the resistance and there was a decrease below 300 K. Subsequent tempering thermal treatment at 653 K (1h) and cooling cause the anomalous reduction of electrical resistance below 320 K and the occurrence of martensitic transformation from B2 to R phase with $T_R=310$ K, independent of x. On the other hand, after 723 K and 823 K tempering, for 1 hour, there was martensitic transformation in two stages, from B2 to R and subsequently B19' (M_s dependent on x and T_A). After tempering at 923 K or above, martensitic transition could no longer be found. The first stage, at 500 K, shows structural changes inducing martensitic phases at low temperatures. The second stage, at 900 K, shows the formation of phase B2 and the disappearance of other phases, causing martensitic transition. Thus, NiTi alloys reveal great dependence on instituted thermal treatment as well as on their composition. As a result, they show one or two stages of martensitic transformation, the first stage related to moving from phase B2 to B19' (monoclinic) and the second stage of martensitic transformation from B2 to R and later to B19'. The R phase is a rhombohedral distortion of the crystalline structure of the B2 towards $(111)_A$.

Compression tests using Instron machine were performed in order to examine the behavior of nickel-titanium coil springs with different geometrical characteristics. The springs were studied at different temperatures (27°C, 37°C and 47°C) and at compression levels varying from 0.5 N to 3.5 N. The influence of sterilization upon the behavior of 0.016 x 0.022-in cross-section wire was examined and the result obtained was that the width of the superelasticity plateaus of different springs moved from 0% to 66% of relative compression. The higher is the temperature, the lower is the plateau hysteresis. The temperature increase from 27°C to 47°C, caused an increase in the height and a shortening in the width of the plateaus. There was no meaningful influence of the process of sterilization upon the behavior of springs. In this way, different behavior standards have been established for the different spring configurations.²⁹

CONCLUSIONS

- Nickel-titanium alloys have shown a growing evolution, from the first samples with distinctive martensitic characteristics until the current ones, with thermoelastic and superelastic (pseudoelastic) properties.
- Many nickel-titanium alloys available as superelastic do not correspond to manufacture's specifications being just less stiff than stainless steel alloys.
- The ideal alloy would be one that presented a TTR which coincided with or which would be really close to the temperature of the buccal cavity (A_f) in order to allow SIM to be formed; one which did not show a shift of TTR because of the stress applied and would have good springback at room temperature; and which showed a small difference between the plateaus (little hysteresis) and the magnitude between the plateaus would be within tension levels compatible with biological dental movement.

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