Pseudoelasticity and thermoelasticity of nickel-titanium alloys: A clinically oriented review. Part I: Temperature transitional ranges

Margherita Santoro, DDS, MA,[a] Olivier F. Nicolay, DDS, MS,[b] and Thomas J. Cangialosi, DDS[c]
New York, NY

The purpose of this review was to organize a systematic reference to help orthodontists evaluate commonly used orthodontic nickel-titanium alloys. Part I of the article reviews the data available in the literature regarding the temperature transitional ranges of the alloys. The thermomechanical behavior of these compounds is, in fact, strictly dependent on the correlation between the temperature transitional range and the oral temperature range. Part II of the article will focus on the mechanical characteristics of the alloys, such as the magnitude of the forces delivered and its correlations with temperature transitional range and oral temperature. (Am J Orthod Dentofacial Orthop 2001;119:587-93)

The engineering of nickel-titanium (NiTi) alloys has made remarkable progress since the original work of Buehler for the Naval Ordinance Laboratory in the early 1960s. Buehler's preliminary results led to development of the first NiTi orthodontic alloy by pioneers such as Andreasen and his colleagues.[1-3]

New and improved materials are constantly being proposed to the orthodontist, and this sometimes increases confusion about the actual characteristics of the wires. In fact, the ubiquitous claims of improved performance are not always supported by correct information about the temperature transitional ranges (TTRs) and the mechanical properties of the wire. Different parameters and experimental settings have been used to analyze the performance of alloys with different compositions and properties, and several classifications have been suggested.[4-9]

Therefore, the aim of this review is to summarize the criteria, validated by data available in the literature, that the orthodontist might use to evaluate current commercial products.

A brief summary of the atomic composition and thermomechanical behavior of NiTi alloys is provided to clarify the theoretical basis of the inquiry. In addition, the importance of properly set TTRs is stressed.

From the Division of Orthodontics at the Columbia University School of Dental and Oral Surgery, New York, NY.
[a]Assistant Professor of Clinical Orthodontics.
[b]Associate Professor of Clinical Orthodontics.
[c]Professor and Chairman.
Reprint requests to: Margherita Santoro, Division of Orthodontics, Columbia University, School of Dental and Oral Surgery, 635 W 168th St, P O Box 20, New York, NY 10032; e-mail, ms190@columbia.edu.
Submitted, January 2000; revised and accepted, April 2000.

0889-5406/2001/$35.00 + 0 **8/1/112446**
doi:10.1067/mod.2001.112446

MECHANICAL PROPERTIES AND COMPOSITION OF NICKEL-TITANIUM ALLOYS

Thermoelasticity and shape memory effect

An ideal NiTi wire should retain a stable predesigned archform at mouth temperature and yet be formable at a lower room temperature. In other words, it should be possible to engage the wire into the brackets during a reasonable time interval, and only later should the wire recover its ideal arch form and apply light, predictable, constant, and continuous force to the dentoalveolar structures.[3] Because of the most recent technological advancements, superelastic NiTi alloys that meet these requirements are finally available.

Superelasticity is determined by the typical crystallographic characteristics of NiTi; the tri-dimensional lattice of the alloy can be present in 2 phases: martensite and austenite. In the martensitic phase, the lattice is body-centered (cubic or tetragonal); in the austenitic phase, it is face-centered (hexagonal close packed). An intermediate rhombohedral "R" phase with a simple hexagonal lattice has also been identified. In response to temperature variations, the crystal structure undergoes deformations in which the molecular arrangement is modified without a change of the atomic composition so that the transformation is diffusionless. The alloys essentially undergo a reorganization to meet the new environmental conditions—a property that has earned them the designation of "smart materials."[10-14] The transformation from the austenitic to the martensitic phase (thermoelastic martensitic transformation) is reversible (pseudoshearing), whereas in metals

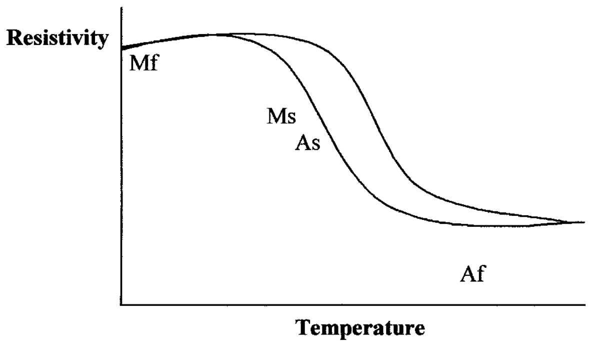

Fig 1. Resistivity/temperature graph for superelastic NiTi alloys. *Mf,* Martensite final; *Ms,* martensite start; *As,* austenite start; *Af,* austenite final.

and other alloys an equivalent amount of stress usually generates an irreversible shearing deformation.[5,12-15]

Each NiTi alloy has a specific temperature range in which the phase transition takes place—the TTR. Ideally, the crystal structure of the alloys should be confirmed by means of either radiographic diffraction or differential scanning calorimetry. However, because austenite and martensite present different amounts of resistance to the passage of electrical currents, it is possible to infer the phase transformation temperatures through the study of resistivity.[14,16,17]

The diagram in Fig 1 illustrates the resistivity of a superelastic NiTi alloy as it relates to the temperature (resitivity/temperature curve). Ms and Mf are the initial and the final temperatures, respectively, at which the martensitic phase is formed; As and Af are the initial and final temperatures for the austenitic phase.

At lower temperatures, the alloy is completely present in the martensitic phase (Mf to Ms) until the increase in temperature causes the progressive transformation into austenite (from Ms to Af). At higher temperatures (beyond Af), the alloy exists exclusively in the austenitic phase.[12-14,18]

An interesting feature of these thermoelastic properties is the so-called *shape memory effect*, which has remarkable clinical applications. Through deflection and repeated temperature cycles, the wire in the austenitic phase is able to "memorize" a preformed shape, including specific orthodontic archforms. By lowering the temperature, the alloy is transformed into martensite and becomes pliable and easily deformed. However, every time the temperature rises above Af to the austenitic phase, the wire will remember and recover the ideal archform. The technical name of the phenomenon is *one-way shape memory effect,* since only 1 of the 2 phases, in this case the austenite, retains a memorized shape.[14,19]

A practical explanatory example of the behavior is a copper NiTi wire thermoactive at 40°C. At room temperature, when the wire is martensitic or in a mixed phase, it is possible to introduce relatively sharp bends in the wire. The original archform will be regained simply by heating the wire in hot water at a temperature above Af, in this specific case, above 40°C.[20]

Shape memory alloys may fulfill the concept of the ideal archwire, but, unfortunately, the presence of the shape memory effect does not necessarily provide low and continuous delivery of forces. In fact, for the memory property to be clinically detectable, the Af of the alloy has to be set slightly below oral temperature so that the wire will be primarily austenitic intraorally and almost completely martensitic extraorally. However, when the alloy is completely transformed into austenite (temperatures above Af), the stress-strain curve follows the regular pattern of other alloys, such as stainless steel, with a direct proportionality between applied stress and resulting strain and basically lacking the typical superelastic plateau. In other words, a NiTi alloy completely transformed into austenite is definitely more elastic than other alloys, but it is not "superelastic," at least in the absence of stress. The superelasticity of NiTi wires is, in fact, correlated to the coexistence of the 2 phases.[21] In Fig 1, in the section of the curve including Ms and Af, the forces leading to a forward and a reverse transformation between the 2 phases are equal. This particular atomic equilibrium gives the NiTi lattice the ability to absorb deflection stresses, and, as a consequence, the modulus of elasticity of the alloy becomes typically low.[12-14] As a general rule, the austenitic phase of a superelastic wire will be stiffer than the martensitic phase, but both will be stiffer than a superelastic wire in phase transition. Therefore, one of the objectives of research in the field should be the creation of new alloys, such as copper NiTi 40°C, with TTRs that correspond to the oral environment temperature and reach Af above the oral temperature. Unfortunately, the "natural charm" of the shape memory effect still holds the interest of manufacturers and clinicians focused on austenitic alloys with Af below oral temperature, whereas characteristics such as magnitude and quality of force delivery have somehow lost priority.

On the other hand, one may wonder if such a rigid evaluation of the superelastic property of the alloys is truly necessary in clinical applications. The performance of any NiTi alloy is strictly influenced by its composition and manufacturing procedures. For example, in theory, it is possible that one specific alloy in its austenitic phase (or even a work-hardened alloy) could deliver a biologically acceptable force, comparable to the force of a superelastic alloy in phase transition, especially when only moderate deflection is necessary. Despite commonly accepted commercial claims, the low values of force delivery of most NiTi alloys are mainly hypothetical and still need to be precisely quantified and compared with the force delivery of other established alloys through properly designed experiments. Other factors, such as stress, also have a strong influence on the phase transformation and, as a consequence, on the forces generated.

Pseudoelasticity

For most orthodontic alloys with an Af below oral temperature, austenite is the prevalent phase intraorally, while only a small percentage of martensite (and the intermediate phase R) is present in the grain structure. Because austenite has relatively higher stiffness compared with the transitional phase, greater quantities of martensite need to form in these austenitic wires to activate the superelastic properties. Somehow, the martensite must form independently of temperature variations, and, fortunately, some help in this regard comes from the application of stress on the austenitic wire. The deflection generates a local martensitic transformation and produces stress-induced martensite (SIM). The highest temperature at which the martensite can form is referred to as Md, and in austenitic alloys Md is usually located above Af and above the oral temperature, allowing the SIM to form in the stressed areas even if the rest of the wire remains austenitic. However, the SIM is unstable, and if the specimen is maintained at oral temperature it undergoes reverse transformation to the austenitic phase as soon as the stress is removed.[14,22] In orthodontic clinical applications, SIM forms where the wire is tied to brackets on misaligned teeth so that the wire becomes noticeably pliable in the deflected areas, with seemingly permanent deformation. Therefore, delivery forces will be lowered in the needed areas only. In those areas, the wire will be superelastic until, after tooth movement, a self-controlled reduction of the deflection will restore the stiffer austenitic phase. In summary, the formation of SIM partially compensates for the lack of a thermally induced martensite and contributes to the superelastic behavior of austenitic NiTi alloys.

This property, termed *pseudoelasticity*, can be considered a localized stress-related superelastic phenomenon.[23-29] However, for the SIM to form, the Af of the alloy can only be slightly lower than the oral temperature.[30] If Af is considerably lower than the oral temperature, the lattice will always have the tendency to reconvert to austenite, and too much energy (in the form of a deflective stress) would be necessary to counteract this tendency and maintain the presence of SIM. Therefore, only in cases of very severe crowding will an austenitic alloy behave superelastically.

Before proceeding to the review of the properties of the commercially available alloys, a few words are needed on some recent investigations as to whether the formation of SIM, as a modification of the lattice, could interfere or modify the temperature range of the phase transformation. Some recent investigations have actually found that SIM generates a shift of the preset TTR of the alloy toward higher temperatures because, as a result of the presence of the mechanical deformation of the lattice, more energy will be required (in this case in the form of heat) to reconvert SIM into austenite. This means that if the values of the TTR provided by the manufacturers are not calculated under proper conditions of deflection, those values might be underestimated and could fail to correspond to the actual TTR values existing in orthodontic applications.[21]

In summary, the pseudoelastic (stress-related) and thermoelastic (temperature-related) behaviors of NiTi alloys are more complex and interdependent than expected. The transformation temperatures provided by the manufacturers, however, are still generally calculated in the absence of deflection, that is, in experimental settings that do not adequately replicate the intraoral environment.

REVIEW OF AVAILABLE ALLOYS

Pseudoelastic and thermoelastic properties are not always present in all commercial orthodontic alloys available on the market. Sometimes the product advertisements can be confusing or even misleading. In this review, we attempt to clarify a few points in this regard, and, we hope, simplify the clinical choice by attributing the correct properties to the most commonly used alloys.

NiTi orthodontic wires are generally classified as superelastic or nonsuperelastic. The original Nitinol, developed in the early 1960s, is a stabilized form of the alloy in which work-hardening has abolished the phase transformation. The alloy does not exhibit a shape memory effect, but the low modulus of elasticity and the high working range make Nitinol useful when considerable deflections are necessary.[1-6,12,14,22]

As a further development of Nitinol, the General Research Institute for Non-ferrous Metals, in Beijing, and the Furukawa Electric Co Ltd, in Japan, later proposed new NiTi alloys of similar composition, named, respectively, Chinese NiTi and Japanese NiTi. The more advanced alloys (now conventionally known as Chinese NiTi) have different transition temperatures than Nitinol and present a phase transformation. Chinese NiTi is austenitic at oral temperature, and, because its TTR is lower than the oral temperature, it is not intended to exhibit pure thermoelastic properties during clinical applications. On the other hand, Chinese NiTi does possess pseudoelastic characteristics under stress because of the formation of SIM.[31-34]

The most recent technological advancements allow the TTR to be set at specific temperatures (27°C, 35°C, 40°C), either through heat treatment and pressure variations (as with CV NiTi; Masel Industries, Bristol, Pa) or through modification of atomic composition. In copper NiTi, for example, the nickel in the alloy has been partially replaced by copper to produce ternary alloys.[14,20]

The classifications of NiTi compounds have evolved with the introduction of new products. Waters' review in 1992 divided the compounds into 3 groups, based on their TTRs: Group 1 included alloys with TTRs between room temperature and body temperature (martensitic active alloys); group 2 included alloys with TTRs below room temperature (austenitic); and group 3 included alloys with TTRs close to body temperature, "which by virtue of the shape memory effect spring back to their original shape when activated by the body heat."[35]

More recently, Evans and Durning[36,37] introduced an even more comprehensive classification of orthodontic alloys, dividing them into 5 groups: (1) phase I, including alloys like gold and stainless steel, (2) phase II, stabilized, (3) phase III, superelastic-active austenitic, (4) phase IV, thermodynamic-active martensitic, and (5) phase V, graded thermodynamic. The stabilized phase II alloys correspond to the original work-hardened Nitinol, whereas the phase III active austenitic is predominantly austenitic at room temperature, with a TTR below the intraoral temperature and thus presents pseudoelastic properties. The phase IV thermodynamic or active martensitic alloys, because of the improved technical ability of dosing the amount of austenite present in the alloys, have a TTR set very close to the intraoral temperature or even corresponding to it. These alloys have a great working range at room temperature; because they exist in a mixed or rhombohedral phase at room temperature, they are able to accept and maintain seemingly permanent deformations. Once exposed to the higher intraoral temperature, both the stress-induced and the temperature-dependent martensite will be gradually converted into austenite, with a recovery of the ideal preset archform and, at the same time, an increase of force delivery.

Included in the active martensitic group are wires with an Af set at a temperature above 37°C, such as copper NiTi 40°C, which is almost completely transformed into martensite during clinical applications. This wire is pliable both intraorally and extraorally, and it will accept bends. The forces exerted on the dentoalveolar structures are remarkably low; therefore, the alloy is recommended for the treatment of patients with periodontal problems. The austenite will form only when the temperature rises above 40°C. It is already common practice to prescribe hot rinses to temporarily increase force delivery to accelerate tooth movement. Conversely, cold rinses will relieve discomfort.[19]

The low stiffness of copper NiTi 40°C also presents the mechanical disadvantage of not allowing for complete dental alignment or full control of transverse dimensions. A second wire with a larger diameter or greater stiffness is usually required.

Temperature transitional ranges of available alloys

Several experiments have been performed in recent years to verify whether the TTRs of orthodontic alloys correspond to the values provided by the manufacturers. As previously mentioned, the TTR of the alloy should be close to, or slightly below, the oral temperature to allow for the formation of SIM.

The intraoral temperature fluctuates widely because of the ingestion of hot and cold food and beverages and because different areas of the oral cavity exhibit different temperatures. Nevertheless, it can be reasonably approximated in experimental settings between 35°C and 37°C.[38-40]

Another source of variation in NiTi experiments is the complexity of the manufacturing procedures. A great variation in wire properties within batches is a common finding that strongly limits the consistency of the experimental data. Wires of similar composition can show very different TTRs, especially when they are manufactured by different companies. As a result, the findings of different experiments are hardly comparable.[28,35] Moreover, some manufacturers provide accurate information about the TTRs of their NiTi products, whereas others do not.

A review of the published data reveals that not all of the NiTi wires available present clinically useful thermal behavior (Table I).

Yoneyama, Doi, and Hamanaka,[29] using differential scanning calorimetry, found that most orthodontic wires have TTRs between 17°C and 32°C. Practically speaking, such wires with the lowest Af are unable to exhibit superelastic behavior during clinical applications.

Reflex wire (TP Orthodontics, La Porte, Ind) presents an Af set at 27°C, and 2 superelastic copper NiTi wires (Copper Ni-Ti; Ormco, Orange, Calif) have Afs set at 27°C and 35°C; such alloys can be safely classified as active austenitic. Heat Activated NiTi alloy (Highland Metals, San Jose, Calif) has an Af set at 68°C and an Mf set at 24°C; this alloy has a considerably extended TTR, and the phase transition is present consistently during clinical applications. 40°C Thermo-Active Copper Ni-Ti (Ormco) can be consid-

Table I. Transitional temperature values of orthodontic NiTi alloys

Product	*Manufacturer*	*TT unloaded*	*TT stress-related*	*References*
Heat Activated NiTi	Highland Metals	24°C-68°C	—	36, 37
Thermomemoria	Leone	Af 24°C	—	36, 37
Reflex	TP Orthodontics	Af 27°C	—	36, 37
Nitinol XL	3M Unitek			
27°C Superelastic Copper Ni-Ti	Ormco	Af 31°C	3 brackets bending test 6-mm deflection Af 33°C	21
35°C Thermo-Active Copper Ni-Ti	Ormco	Af 33°C	3 brackets bending test 6-mm deflection Af 39°C	21
40°C Thermo-Active Copper Ni-Ti	Ormco	Af 39°C	3 brackets bending test 6-mm deflection Af 39°C	21
Sentalloy	GAC	Af 22°C	28°C	22, 23
Neo Sentalloy	GAC	Af 28°C	36°C	22, 23, 27, 41
Nitinol Heat Activated	3M Unitek	Af 36°C	3 brackets bending test 6-mm deflection Af 38°C	21

ered truly superelastic at oral temperature. The Af of Sentalloy (GAC International, Islandia, NY) is approximately 28°C in the absence of loading.[21,25,27] Other manufacturers generally claim an Af set at a nominal oral temperature, approximately 35°C.[12,17]

Stress-related TTRs

It has been demonstrated for some NiTi alloys that the formation of SIM generates a shift of the TTR toward higher temperatures. This phenomenon is due to the fact that the application of stress—in this case, in the form of a deflection—maintains the atomic configuration of martensite at the expense of austenite. Higher energy (heat, for example) will then be required to reconvert the SIM into austenite. From a clinical point of view, the stress-related TTR, or, more simply, the stress-related Af, is the actual temperature at which thermoactive wires will be "activated." The stress-related Af is, in fact, the temperature at which stressed wires, tied to the brackets, will be transformed from the low-stiffness martensite to the higher-stiffness austenite and will deliver a greater force to the dentoalveolar stuctures. The immediate clinical advantage of the stress-generated increase of Af is, of course, better preservation of SIM and of pseudoelastic properties, but the phenomenon also points out the necessity of studying the TTR of orthodontic wires in the presence of stress. Fortunately, the data available in the literature are usually gathered through experiments that try to reproduce a clinical setting and involve the application of stress in various forms. Table I summarizes some data on the TTRs of commercial orthodontic alloys.

Mullins, Bagby, and Norman[17] analyzed Neo Sentalloy F100, F200, F300, and Bioforce Sentalloy (GAC) with a deflection device that reproduced the loading of a maxillary lateral incisor. At 5°C, all of the alloys were martensitic because they accepted a pseudo-permanent deformation of 2.38 mm. However, at 37°C, the permanent deformation under stress averaged only 0.08 mm, with no statistically significant differences between the alloys. The alloys were completely transformed into austenite at 37°C.[17]

Coluzzi et al[27] compared the stress-related Af to the Af of Neo Sentalloy F200 and Thermomemoria (Batch C 8922-16; Leone, Oxnard, Calif). The authors performed a temperature cycle on the alloys with deflection and in the absence of deflection. In the absence of deflection, Neo Sentalloy exhibited an Af of 28°C. Af increased proportionally with loading to a maximum of 34°C. Leone's wire had an Af in unloaded conditions set at 20°C and increased to a maximum of 35°C with loading.

Bishara et al[41] compared the thermodynamic properties of Active Arch Nitinol (3M Unitek, Monrovia, Calif), Heat-Activated Nitinol (Ortho Arch, Hoffman Estates, Ill), and Neo Sentalloy. The experimental setting was a variation of a cantilever bend test in a temperature-controlled environment. Bends of 30° to 40° were introduced in straight segments of the wires, and the samples were then immersed in a water bath. All of the samples showed 100% recovery of their original shape. Active Arch Nitinol presented a TTR between 22.4°C and 28°C; Heat-Activated Nitinol had a TTR between 23°C and 26.5°C, and Neo Sentalloy had a TTR between 21°C and 28°C. Therefore, all the samples presented a TTR below oral temperature.[41]

In addition to Sentalloy and analogous austenitic alloys, some of the new so-called thermoactive NiTi alloys have also been studied under stress.

Santoro and Beshers[21] tested Neo Sentalloy, 27°C Superelastic Copper Ni-Ti (Ormco), 35°C and 40°C

Thermo-Active Copper Ni-Ti, and Active Arch Nitinol (3M Unitek). The experimental setting reproduced the clinical loading of a crowded lower incisor. In agreement with previous studies, Neo Sentalloy was found to be sensitive to loading, showing a stress-related Af of 28°C, which agrees with previous studies. 27°C Superelastic Copper Ni-Ti had a higher stress-related Af of 32°C. Therefore, both the alloys were mainly austenitic intraorally even in the presence of deflection. 35°C Thermo-Active Copper Ni-Ti had a stress-related Af set at 39°C, while 40°C Thermo-Active Copper Ni-Ti presented an Af above oral temperature; it was not influenced by stress but rather displayed predictable stress-related behavior. Thus, it can be considered a true thermoelastic wire.[21]

SUMMARY AND CONCLUSIONS

Two concomitant phenomena are responsible for the superelastic behavior of orthodontic NiTi alloys: a temperature-related phase transformation along a TTR (thermoelasticity), and the formation of SIM in localized areas of the archwire due to deflection (pseudoelasticity). The shape memory effect is derived from the thermoelastic transformation from martensite to austenite, and orthodontic clinical application requires setting the TTR of the alloys slightly below oral temperature. This type of thermoelastic alloy, however, will be completely austenitic at oral temperature, and the austenite presents a higher modulus of elasticity that results in a greater stiffness of the wire. In austenitic alloys, the formation of SIM will guarantee the presence of the superelastic behavior necessary for the release of light and continuous forces.

Therefore, the Af of the alloy should not be set at a temperature considerably below oral temperature or the formation of SIM will not occur. It would actually be advisable to evaluate alloys on the basis of their stress-related TTRs because the application of stress usually raises the Af of the alloy.

According to the data available in the literature, most of the commercially available superelastic wires exhibit stress-related Afs ranging from 22°C to 28°C, and the TTRs of thermoelastic wires are set at higher temperatures, from 35°C to 40°C.

In summary, 2 fundamental properties should be taken into account to make an educated selection of a NiTi wire: (1) a proper stress-related TTR, corresponding to or slightly below oral temperature and (2) a low deactivation force released to the dentoalveolar structures to prevent deleterious side effects, such as pain after bone hyalinization and possible root resorption. This mechanical characteristic will be more extensively considered in the second part of this review.

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