Original article

Phase transformation analysis of varied nickel-titanium orthodontic wires

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Keywords: *phase transformation; nickel-titanium; differential scanning calorimetry; shape memory*

Background The shape memory effect of nickel-titanium (NiTi) archwires is largely determined by the phase transition temperature. It is associated with a reversible transformation from martensite to austenite. The aim of this study was to characterize austenite, martensite and R phase temperatures as well as transition temperature ranges of the commonly used clinical NiTi orthodontic arch wires selected from several manufacturers.

Methods Differential scanning calorimetry (DSC) method was used to study the phase transformation temperatures and the phase transition processes of 9 commonly used clinical NiTi alloys (types: 0.40 mm (0.016 inch), 0.40 mm × 0.56 mm (0.016 inch × 0.022 inch)).

Results The austenite finish temperatures (Af) of 0.40 mm Smart, Ormco and 3M NiTi wires were lower than the room temperature, and no phase transformation was detected during oral temperature. Therefore, we predicted that these types of NiTi did not possess shape memory property. For 0.40 mm and 0.40 mm × 0.56 mm Youyan I NiTi wires, no phase transformation was detected during the scanning temperature range, suggesting that these two types of wires did not possess shape memory either. The Af of 0.40 mm × 0.56 mm Smart, L&H, Youyan II Ni-Ti wires were close to the oral temperature and presented as martensitic-austenitic structures at room temperature, suggesting the NiTi wires listed above have good shape memory effect. Although the 0.40 mm × 0.56 mm Damon CuNiTi wire showed martensitic-austenitic structures at oral temperature, its Af was much higher than the oral temperature. It means that transformation from martensite to austenite for this type of NiTi only finishes when oral temperature is above normal.

Conclusion The phase transformation temperatures and transformation behavior varied among different commonly used NiTi orthodontic arch wires, leading to variability in shape memory effect.

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Nickel-Titanium (NiTi) alloy archwires have been used widely in clinical orthodontic treatment because of their extraordinary properties of shape memory and super-elasticity.[1-3] NiTi alloy has two different temperature-dependent crystallographic structures,[4,5] i.e. austenite at higher temperatures and martensite at lower temperatures. This temperature-dependent phase transformation is from austenite to martensite during cooling, while the reverse transformation from martensite to austenite starts upon heating.[6]

Shape memory refers to the ability of certain materials that "remember" their original shapes even after severe deformations. NiTi alloys is one of the main types of alloys that possess such shape memory properties, e.g. after a sample of NiTi alloys has been deformed from its original crystallographic configuration at low temperatures (martensitic phase), it regains its original geometry by itself during heating (austenite). The shape memory property of NiTi alloys has, therefore, been utilized in arch wires to straighten dentition.

The shape memory effect of NiTi archwires is largely determined by the phase transition temperature.[7] When the phase transition temperature of a NiTi arch wire is close to oral temperature, the yield strength of shape memory could be up to maximum. There are dozens of NiTi archwires with different brand names currently on the chinese market. No real transformation temperature is provided for some of the products. While for other products that provide phase transformation properties though, they can not be properly compared because the measuring conditions and specifications differ from one manufacturer to another.

In view of this, we conducted Differential Scanning Calorimetry (DSC) tests on 9 different kinds of 0.40 mm × 0.56 mm (0.016 inch × 0.022 inch) and 0.40 mm (0.016 inch) NiTi alloy wires to determine their properties. The aim of our current study was to investigate the phase transformations and phase temperature of different kinds of NiTi alloys with DSC and gave orthodontics with a guideline on choosing proper NiTi alloy archwires with special goals of treatment. Furthermore, our study provided a theoretical basis for the research of mechanical properties of shape memory alloys.

METHODS

The transformation behavior and the phase temperature were determined by thermal analyses (differential scanning

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Table 1. NiTi orthodontic wires investigated in present study

Products	Dimension (mm)	Manufactures	Call for short
Smart SE	0.40	Beijing Smart Tech Co., Ltd.	Smart
Kleen PakR™ NI-TI	0.40	Ormco, Glendora, Calif	Ormco
CY16	0.40	Grikin Advanced Materials Co., Ltd	Youyan I
Nitinol heat-Activated	0.40	3M Unitek , Monrovia, Calif	3M
Smart SE	0.40×0.56	Beijing Smart Tech Co., Ltd	Smart
Damon CuNiTi	0.40×0.56	Ormco, Glendora, Calif	Damon
L&H Titan	0.40×0.56	Tomy International	L&HR
CF1616	0.40×0.56	Grikin Advanced Materials Co., Ltd	Youyan I
RF1616	0.40×0.56	Grikin Advanced Materials Co., Ltd	Youyan II

calorimetry, DSC; Q100 TA instrument, USA) in the temperature range from –80°C to +80°C. Nine nickel-titanium orthodontic wires with cross-section dimension of 0.40 mm × 0.56 mm and 0.40 mm were selected in the study (Table 1).

The occlusal-gingival and buccal-lingual dimensions were measured with micrometer gauge. The length of each wire specimen was 5 mm. They were carefully cut with a water-cooled, slow-speed diamond saw to minimize mechanical stresses that might change the proportions of the austenitic and martenditic NiTi phases from those in the as-received wires.

Three measurement runs were performed per sample, with a heating and cooling rate of 10 K/min. Each test sample consisted of 3 segments placed in an open aluminum pan with dry nitrogen gas used to flush the specimen chamber, preventing condensation of water vapor and oxidation of NiTi wires.

The amount of heat released or absorbed during phase transformation was recorded as a function of temperature. At the same time, the transition temperatures (austenite start, As; austenite finish, Af; martensite start, Ms; martensite finish, Mf; rhombohedral start, RS; rhombohedral finish, Rf) were determined according to Q100 TA using the software of origin7.1 (Figure 1). The start and finish temperatures of each phase transformation were determined from tangent lines where the DSC curve deviates from the adjacent baselines. R phase indicates that NiTi alloy possesses the ability of two-way memory effect.

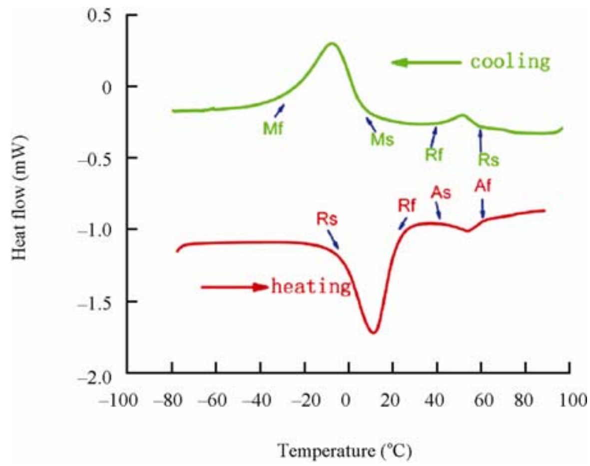

Figure 1. DSC heating and cooling curves. The green heat-flow curves for cooling cycle and the red heat-flow curves for heating cycle. Ms: martensite start; Mf: martensite finish; As: austenite start; Af: austenite finish.

RESULTS

Transformation process and the phase temperatures of different 0.016 inch NiTi sample wires

Tables 2, 3 and Figure 2 show the transformation behavior and the phase temperatures of different NiTi round wires. The Af of Smart, Ormco and 3M NiTi round wires were lower than the room temperature, and no phase transformation was dectected during oral temperature, indicating that these types of NiTi examined do not possess the shape memory property. Interestingly we can see R phase during the cooling curve for 3M type, and R phase during the heating curve for Ormoco type NiTi wires.

There were no phase transformations detected for Youyan I round NiTi wires during the scanning temperature range from –80°C to +80°C.

Transformation behavior and the phase temperatures of different 0.40 mm × 0.56 mm NiTi wires

Tables 2, 4 and Figure 3 show the transformation behavior and the transition temperatures of different NiTi rectangular wires. The AF of Smart, L&H, Youyan II NiTi rectangular wires were close to the oral temperature. At room temperature the phase were the mixture of martensite and austenite, which switched to austenite phase in the oral temperature, suggesting that these types of NiTi wires posses the shape memory effect.

No phase transformation detected for Youyan I NiTi rectangular wires during the scanning temperature range, suggesting it has no shape memory effect.

Although the 0.40 mm × 0.56 mm Damon CuNiTi wire showed martensitic-austenitic structures at oral temperature, its Af was much higher than the oral temperature. It means that transformation from martensite to austenite for this type of NiTi finishes when oral temperature is above normal, suggesting the yield stress can not reach maximum under normal oral temperature.

DISCUSSION

Methods of transformation temperature analyses

The common methods of analysis transformation include Differential Scanning Calorimetry analyses, X-ray diffraction analyses, Electrical Resistivity analysis and Dynamic Mechanical analysis.

Table 2. Transformation temperature of NiTi orthodontic wires (°C)

Products	Cooling				Heating			
	Rs	Rf	Ms	Mf	Rs	Rf	As	Af
0.40 mm								
3M	21.85	2.49	–48	–	–	–	2.06	22.53
Ormco	–	–	18.67	4.70	–7.84	9.73	9.87	21.89
Smart	–	–	18.61	6.66	–	–	10.3	22.43
Youyan I	–	–	–	–	–	–	–	–
0.40 mm×0.56 mm								
L&H	31.51	19.75	–17.88	–30.82	–6.31	20.35	21.68	36.61
Damon	59.83	39.81	6.34	–28.55	–4.15	22.15	40.67	61.46
Smart	10.9	1.9	–44.3	–	–8.1	11.13	13.76	34.32
Youyan I	–	–	–	–	–	–	–	–
Youyan II	30.57	24.45	–48.26	–	13.01	28.62	29.13	38.49

Table 3. Transition behavior of NiTi round wire

Archwires		Phase transformation
Smart	Heating: M→A	Without R-phase transition
	Cooling: A→M	
3M	Heating: M→A	With R-phase transition
	Cooling: A→R→M	
Ormco	Heating: M→R→A	With R-phase transition
	Cooling: A→M	
Youyan I	Heating:--------------	With no transition in the temperature range
	Cooling:--------------	

Table 4. Transition behavior of NiTi rectangular wire

Archwires		Phase transformation
Smart	Heating: M→R→A	With R-phase transition
	Cooling: A→R→M	
Damon CuNiTi	Heating: M→R→A	With R-phase transition
	Cooling: A→R→M	
L&H	Heating: M→R→A	With R-phase transition
	Cooling: A→R→M	
Youyan I	Heating: -------------	With no transition in the temperature range
	Cooling: -------------	
Youyan II	Heating: M→R→A	With R-phase transition
	Cooling: A→R→M	

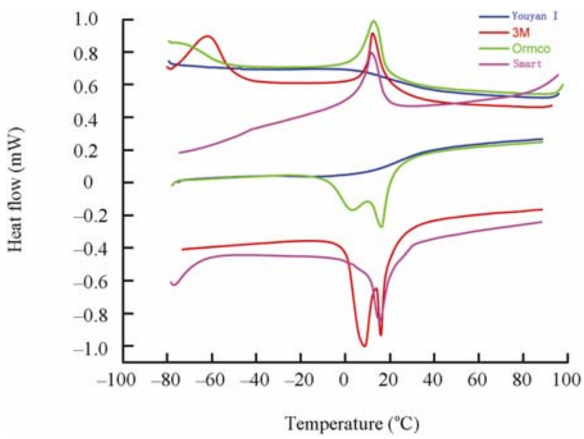

Figure 2. Transition behavior of NiTi round wire

Differential Scanning Calorimetry measures the amount of energy (heat) absorbed or released by a sample as it is heated or cooled.[8] Typical applications include determination of melting point temperature and the heat of melting; measurement of the glass transition temperature; curing and crystallization studies; and identification of phase transformations. Different crystal phases of NiTi alloys have different melting point and the melting heat.

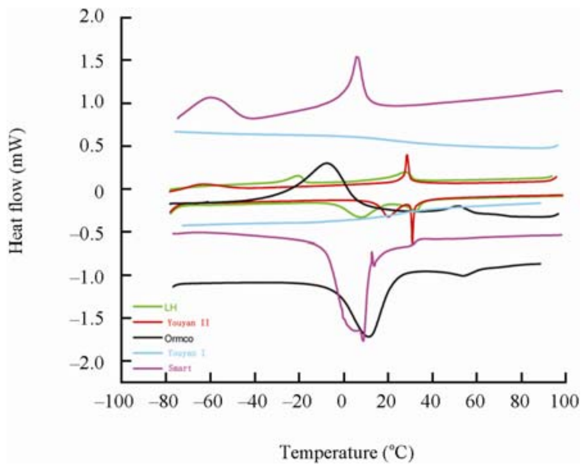

Figure 3. Transition behavior of NiTi rectangular wire.

X-ray diffraction analyses of the nickel-titanium orthodontic wires provide very useful information about the presence of the martensitic and austenitic NiTi phases. But this technique only examines the sample volume within less than about 50 µm of the surface, whereas DSC procides information about the bulk sample.[9,10]

Electrical resistivity measurements has also been employed to investigate the phase transformations in the nickel-titanium orthodontic wires, but this technique does not provide information about the enthalpy changes associated with the transformations.[11,12]

Dynamic mechanical analyses measures the stiffness and damping properties of a material. Damping is expressed in terms of enthalpy and is related to the amount of energy a material can store. DMA is the most sensitive technique for monitoring relaxation events, such as temperature transitions, but it is very expensive.[13]

Shape memory effect and Af

When the temperature was below martensite finish, the phase of NiTi wire was martensite. Putting such wire into the oral, with the temperature rising up to austenite start, the martensite phase was turned to austenite. The wire has the ability to regain its original shape. Therefore, transformation process will take place during oral temperature range.

When NiTi wires were heated, the martensite was partially turned to austenite, and then fully austenite. As and Af are the initial and final temperature for the formation of the austenitic phase during heating. At higher temperatures than Af, the alloy consists exclusively of austenite.

The intraoral temperature widely fluctuates because of the ingestion of hot or cold food and beverage. Furthmore, different areas of oral cavity exhibit different temperatures. Nevertheless, it can be reasonably approximated in experimental settings between 35°C and 37°C if we considere the environmental temperature as 25°C.[14]

The analysis of the curves obtained for Smart, Ormco and 3M Unitek NiTi round wires reveals the Af lower than the environmental temperature. The alloy was completely austenite at room temperature. When put such wires in oral cavity, no phase transformation will take place, suggesting these types of NiTi wiries did not possess the shape memory property required in the clinical use.

When the Af is close to the oral temperature,[15,16] the crystal phase of NiTi alloy is the mixture of martensite and austenite. The wire was pliable and easily deformed. The orthodontic could put such wire into crowded dentition easily.[17] With the increase of the temperature in the oral cavity, phase transition will take place, the martensite phase starts change to the austenite phase. The wire turn harder with shape memory and then yield force to align the dentition. In Smart, L&H, Youyan II NiTi rectangular wire wires, Af were close to the oral temperature. These wires, based on our analysis, had phase transition at oral temperature and possessed the shape memory effect.

In Damon CuNiTi NiTi rectangular wire, Af was about 61.46°C; this value was far higher than the normal oral temperature. It was almost completely martensite during clinical applications and it was pliable both intraorally and extraorally. The forces exerted on the dentoalveolar structures are remarkable low. 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.Therefore, the alloy could be recommended for the treatment of patients with periodontal problems.[15]

Clinical classifications of NiTi wires

We always divided NiTi wires into 4 groups according to their specific transitional temperatures: (1) phase I, work-hardened (2) phase II, superelastic-active austenitic and (3) phase III, thermodynamic-active martensitic and (4) phase IV, graded thermodynamic.[16]

In this study, no phase transformation detected for Youyan I NiTi wires during the scanning temperature range. These work-hardened wires did not exhibit shape memory effect with stabilized forms. But the low modulus of elasticity and the high working range could make them useful when considerable deflections were necessary.[11,15]

Smart, Ormco, 3M Unitek NiTi round wires were superelastic-active austenitic with Af below the room temperature, and thus present no shape memory effect. Mechanical properties tests need to be done to determine whether they possess pseudoelastic properties. Some manufactures claimed their NiTi products have shape memory, but our DSC analysis showed the opposite results to what they claimed. Further investigation is needed to determine the possible reasons for this discrepancy.

Smart, Youyan II NiTi rectangular wires have Af very close to the intraoral temperature. They were thermodynamic and active martensitic alloys, and have a great working range at room temperature, since they exist in a mixed or rhombohedral phase at room temperature. Once these wires were exposed to the higher intraoral temperature, martensite will be gradually converted into austenite with a recovery of the ideal preset arch form, and, at the same time, an increase of force delivery. They were so-called heat-activated NiTi alloys.

Damon CuNiTi NiTi rectangular wire had an Af higher than the intraoral temperature. With hot water, martensite will be gradually converted into austenite and deliver force to align the dentition. They were heat-activated NiTi alloys too.

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