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# An evaluation of the transition temperature range of super-elastic orthodontic NiTi springs using differential scanning calorimetry

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SUMMARY Differential scanning calorimetry (DSC) was used to determine the transition temperature ranges (TTR) of four types of super-elastic orthodontic nickel–titanium coil springs (Sentalloy). A knowledge of the TTR provides information on the temperature at which a NiTi wire or spring can assume superelastic properties and when this quality disappears. The spring types in this study can be distinguished from each other by their characteristic TTR during cooling and heating. For each tested spring type a characteristic TTR during heating (austenite transformation) and cooling (martensite transformation) was evaluated. The hysteresis of the transition temperature, found between cooling and heating, was 3.4–5.2 K. Depending on the spring type the austenite transformation started (As) at 9.7–17.1°C and finished (Af) at 29.2–37°C. The martensite transformation starting temperature (Ms) was evaluated at 32.6–25.4°C, while Mf (martensite transformation finishing temperature) was 12.7–6.5°C.

The results show that the springs become super-elastic when the temperature increases and As is reached. They undergo a loss of super-elastic properties and a rapid decrease in force delivery when they are cooled to Mf. For the tested springs, Mf and As were found to be below room temperature. Thus, at room temperature and some degrees lower, all the tested springs exert super-elastic properties. For orthodontic treatment this means the maintenance of super-elastic behaviour, even when mouth temperature decreases to about room temperature as can occur, for example, during meals.

## Introduction

The discovery of shape memory in nickel–titanium (NiTi) alloys triggered a search for possible technical applications of that phenomenon and led to further exploration of the properties of such alloys (Duerig *et al*., 1982). Subsequently, due to their special properties, NiTi alloys were also introduced in the field of orthodontics (Andreasen and Hilleman, 1971).

The shape memory effect of NiTi alloys is thought to be caused by the occurrence of two crystal modifications, called austenite (high temperature phase) and martensite (low temperature phase), which can be changed back and forth through variations in temperature. Transition is induced over a range of temperature called the ‘transition temperature range’ (TTR; Andreasen *et al*., 1985). At this range both crystal forms exist in a dynamic equilibrium (Drescher, 1990). The two phases are characterized by different physical properties. Martensitic wires are highly ductile and may be plastically deformed. When heated to its TTR, such a deformed wire returns to its original shape (shape memory). The material becomes relatively rigid and unyielding (Andreasen *et al*., 1985). Some newer orthodontic wires exhibit a further unique property, termed ‘super-elasticity’. This is the ability of a wire to exert fairly constant stress values during deformation over a wide range (Miura *et al*., 1986, 1988). Super-elasticity is a stress-induced phenomenon. Bending a super-elastic wire in its austenitic phase creates a martensitic transformation that is reversed when strain is reduced. Super-elastic behaviour only occurs at temperatures above the TTR. To make use of the super-elastic properties of NiTi alloy for a certain application it is necessary to know the temperature range at which transition takes place. For orthodontic wires this means that a TTR must be chosen which lies below body temperature and which guarantees maintenance of the super-elastic properties even at fluctuating temperatures, such as the oral environment.

Prior to martensitic transformation another transition occurs in some NiTi alloy systems under certain conditions, namely R-phase transition (Otsuka, 1992; Filleul and Jordan, 1997). For identifying structural transformation such as R-phase or martensitic transformation, differential scanning calorimetry (DSC) is a useful technique (Filleul and Jordan, 1997). DSC was used in the present study to examine Japanese NiTi alloy (Sentalloy). No indication was found for the existence of three phases (martensite, R-phase, austenite) at the tested temperature range of –20–50°C. Thus, the transformation sequence austenite to martensite on cooling, and martensite to austenite on heating is assumed as described by Miura *et al*. (1986).

NiTi wires are used to fabricate orthodontic coil springs. In this study, super-elastic Japanese NiTi closed coil springs were tested. The force delivery of those springs at changing temperatures, simulating fluctuations in mouth temperature during eating and drinking, was explored in an earlier investigation, but no precise definition of the TTR was carried out (Barwart, 1996). A knowledge of the TTR provides information as to the temperature at which the springs assume super-elastic properties and when this property is lost. It was the aim of the present study to evaluate the TTR of the tested springs by using DSC.

## Materials and methods

Four types of standard Japanese NiTi closed coil springs (Sentalloy, GAC, Central Islip, NY) were used for the test. The spring types differed in force delivery as follows: 50 g (extra light, EL), 100 g (light, L), 150 g (medium, M), and 200 g (heavy, H).

After removing the eyelets each spring was weighed exactly to ±0.01 mg and placed in an aluminium pan. The weight of such a prepared spring was about 8–15 mg (see Table 1). The pans were sealed and placed in the measuring chamber of a differential scanning calorimeter (DSC-7, Perkin Elmer, Norwalk, CT, USA), which was equipped with a device for controlled cooling (CCA-7, Perkin Elmer). Nitrogen was used as the purge gas. After heating the specimens to 60°C, they were cooled (5 K/min) to –20°C for measuring. This temperature was held for 5 minutes and then raised again (5 K/min) to 60°C. In a pre-study two springs of each type were tested, once using only one segment of a spring, then observing the effect of different heating and cooling rates (1, 5, 10 K/min). Data processing was carried out by using 7 Series/Unix DSC-7 Lab System software (Perkin Elmer). For temperature calibration, indium (m.p. 156.4°C) and water were used. Calibration of the DSC signal was performed with indium 99.999 per cent (Perkin Elmer).

Figure 1 shows the cooling and heating curve of the type L spring (light). The start and the end of the transition (onset, offset) were determined as the intersections of a base line and the tangents to each peak. The points As and Ms (austenite/martensite transformation starting temperature) are regarded as the beginning (onset) of the phase transformation, and points Af and Mf (austenite/martensite transformation finishing temperature) as the end of the transformation (offset; Miura *et al*., 1988; Yoneyama, 1992). The heat of transition is represented by the area below the curves.

## Results

The DSC curves of the tested spring types are given in Figure 2. Heating the samples produced an endothermic peak, and cooling created an exothermic peak. Different heating and cooling rates (1, 5, 10 K/min) had little influence on the TTR. Table 1 shows the data obtained. The most distinct peaks were found for the EL type spring and the least pronounced for the H type.

**Table 1** Results from the DSC evaluation of the four types of NiTi closed coil springs tested.

| | Spring type | | | |
|---|---|---|---|---|
| | EL | L | M | H |
| Sample mass (mg) | 8.43 | 13.51 | 14.12 | 12.99 |
| DSC (cooling) | | | | |
| Exothermic peak (°C) | 16.1 | 20.6 | 15.2 | 21.3 |
| Ms (onset, °C) | 25.4 | 29.8 | 28.4 | 32.6 |
| Mf (offset, °C) | 11.8 | 11.6 | 6.5 | 12.7 |
| Heat of transition (J/g) | –1.51 | –1.05 | –0.92 | –0.39 |
| TTR (Ms-Mf, K) | 13.6 | 18.2 | 21.9 | 19.9 |
| DSC (heating) | | | | |
| Endothermic peak (°C) | 20.5 | 24.6 | 18.6 | 26.5 |
| As (onset, °C) | 17.1 | 15.2 | 9.7 | 16.0 |
| Af (offset, °C) | 29.2 | 34.7 | 33.0 | 37.0 |
| Heat of transition (J/g) | 1.49 | 1.08 | 1.05 | 0.77 |
| TTR (As-Af, K) | 12.1 | 19.5 | 23.3 | 21.0 |
| Difference of peaks (exotherm/endotherm, K) | 4.4 | 4.0 | 3.4 | 5.2 |
| Difference of amounts of enthalpy (exotherm/endotherm, J/g) | –0.02 | 0.03 | 0.13 | 0.38 |

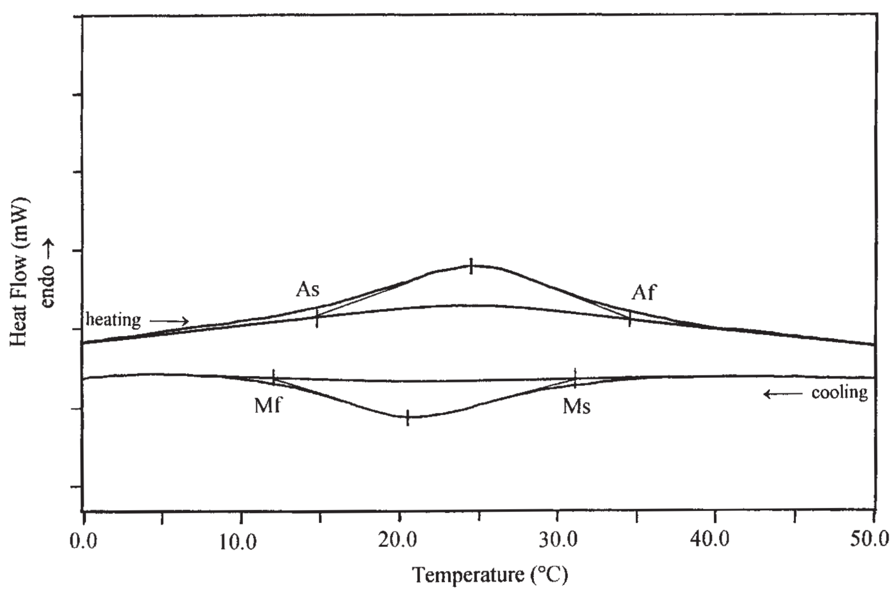


**Figure 1** DSC curves of spring type L at cooling and heating. As, Ms, Af, Mf = austenite/martensite transformation starting/finishing temperature.

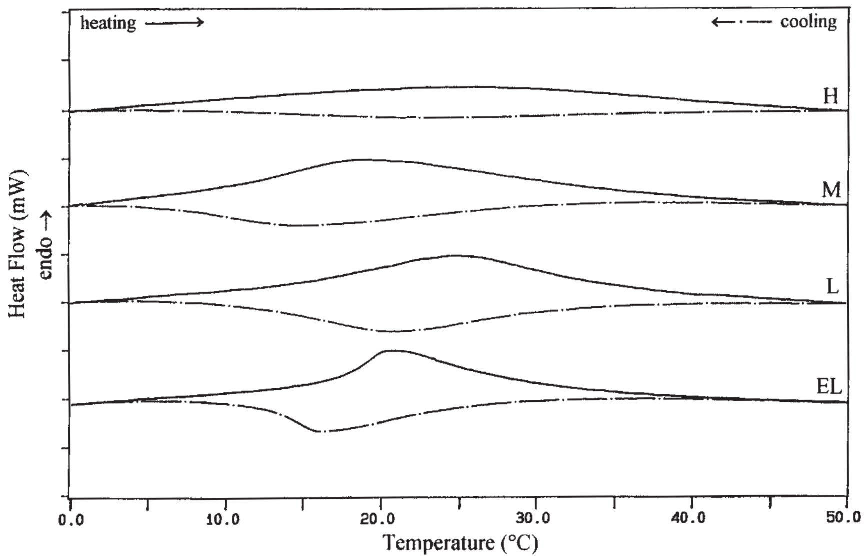


**Figure 2** DSC curves of the tested NiTi coil springs EL, L, M, H.

Accordingly, the values of positive and negative heat of transition decreased from EL to L, to M and to H. As was located below room temperature for all the springs (9.7–17.1°C). Martensitic transformation started (Ms) when the springs were cooled below body temperature (32.6–25.4°C).

For each spring the TTR of austenite transformation differed from the martensite transformation temperature range. Phase transformation was extended over a temperature range up to 23.3 K, depending on the spring type.

## Discussion

Like stainless steel (Khier *et al.*, 1988), NiTi alloys have a two-phase structure comprising an austenitic and a martensitic phase, which affect the properties of these metals. The body-centred cubic crystal lattice (CsCl type B2 structure) of the austenitic phase (Miura *et al.*, 1988) is thought to be the reason for the high spring-back properties of austenitic NiTi wires. When martensitic transformation is induced by cooling or mechanical stress, the lattice changes to a close-packed hexagonal type. This is characterized by symmetrical structures, called martensite twins (Drescher, 1990), which can slide easily against each other. This explains the behaviour of martensitic wires in terms of plastic deformation. Such a deformed wire can regain its original shape when it is transformed to the austenitic phase by heating it to its TTR (shape memory effect). Another characteristic associated with phase transformation is the super-elastic behaviour of some NiTi alloys. The phenomenon of superelasticity seems to be closely related to the energetic processes occurring at transformation (Miura *et al.*, 1988).

The energetic processes of transformation can be demonstrated through differential scanning calorimetry. The DSC curves of the tested springs show that transition of the body-centred cubic lattice (austenite type) to the close-packed hexagonal lattice (martensite type) involves an exothermic reaction. Heating of the martensitic phase, which is thermodynamically stable at low temperatures, creates an endothermic transformation to the austenitic phase. Such a type of reversible transformation is termed 'enantiotropism'. For the tested springs, phase transformation at heating and cooling was characterized by a hysteresis of the transition temperature. This hysteresis is relatively small (3.4 to 5.2 K; see difference of peaks in Table 1) when compared with other enantiotropic crystal modifications, e.g. with organic molecular crystals (Burger and Ramberger, 1979a), but it is sufficiently large to permit co-existence of both crystal modifications at room temperature. Interestingly, DSC examination showed little influence on the TTR of the rate of temperature increase. This characteristic is contrary to the behaviour usually observed in solid-solid transitions (Burger and Ramberger, 1979b).

The As temperature of all the tested springs was found to be below room temperature, while Af was 37°C or lower, depending on the spring type. Martensite transformation started at temperatures not much below body temperature and finished (Mf) between 6.5 and 12.7°C (Table 1). Thus, at room temperature martensitic and austenitic phase are co-existent. Earlier investigations have found superelastic behaviour of the springs at room temperature (Barwart, 1996; Melsen *et al*., 1994). This means that the formation of stress-induced martensite starts after the As point has been reached. The springs become super-elastic at As at increasing temperature and maintain their super-elastic properties until Mf has been reached at cooling.

To make use of the characteristics of NiTi alloys for a particular application a TTR has to be chosen in accordance with the desired effect. The TTR can be modified both by varying the nickel content of the alloy (Andreasen *et al*., 1985) or by heat treatment (Miura *et al*., 1988). Nitinol has a TTR which lies considerably above body temperature (Hurst *et al*., 1990). Thus, at mouth temperature the wire is martensitic. Through mechanical treatment such a wire can become highly elastic (work-hardened martensite), a characteristic that is used for orthodontic treatment (Drescher, 1990). Other NiTi alloys with a TTR at about body temperature, were developed to use the memory effect for orthodontic applications (Andreasen, 1980). Shape memory of NiTi alloys is also used for appliances, such as thermal switches or thermal protection devices, which work at different temperatures (Duerig *et al*., 1982), requiring individual transition temperature ranges.

## Conclusion

To make use of the super-elastic properties of NiTi wires and springs for orthodontic treatment, a TTR below body temperature is required. Furthermore, the TTR should be set low enough to also provide super-elastic behaviour at fluctuating mouth temperatures. Michailesco (1995) found that the tooth surface cooled to 21.3°C during eating and drinking. Lower temperatures (4.3°C) were only measured when ice cubes were in contact with the teeth. When the Mf point of a NiTi alloy is reached at cooling, the alloy becomes fully martensitic. This results in the loss of super-elasticity in NiTi wires and springs, and in a reduction in force delivery to almost zero. As a consequence orthodontic forces will act on an interrupted, rather than continuous basis at varying temperatures. Evaluation of the TTR in this study reveals, that the Mf points of the tested super-elastic NiTi springs are distinctly lower (12.7°C or less) than the mouth temperatures recorded during eating and drinking. Such fluctuations in mouth temperature will not therefore result in a loss of super-elastic behaviour or force delivery. However, the springs will not exert a constant force at fluctuating mouth temperatures because the spring force can change significantly by only minimal variations in temperature, as demonstrated in an earlier study (Barwart, 1996).

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