International Endodontic Journal

doi:10.1111/j.1365-2591.2009.01563.x

Effect of heat treatment on transformation temperatures and bending properties of nickel–titanium endodontic instruments

Y. Yahata[1], T. Yoneyama[2], Y. Hayashi[1], A. Ebihara[1], H. Doi[3], T. Hanawa[3] & H. Suda[1]

[1]Pulp Biology and Endodontics, Department of Restorative Sciences, Graduate School, Tokyo Medical and Dental University, Tokyo, Japan; [2]Department of Dental Materials, Nihon University School of Dentistry, Tokyo, Japan; and [3]Department of Metallurgy, Division of Biomaterials, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Tokyo, Japan

Abstract

Yahata Y, Yoneyama T, Hayashi Y, Ebihara A, Doi H, Hanawa T, Suda H. Effect of heat treatment on transformation temperatures and bending properties of nickel–titanium endodontic instruments. *International Endodontic Journal*, **42**, 621–626, 2009.

Aim To investigate the effect of heat treatment on the bending properties of nickel–titanium endodontic instruments in relation to their transformation behaviour.

Methodology Nickel–titanium super-elastic alloy wire (1.00 mm Ø) was processed into a conical shape with a 0.30 mm diameter tip and 0.06 taper. The heat treatment temperature was set at 440 or 500 °C for a period of 10 or 30 min. Nonheat-treated specimens were used as controls. The phase transformation behaviour was examined using differential scanning calorimetry. A cantilever-bending test was used to evaluate the bending properties of the specimens. Data were analyed by ANOVA and the Tukey–Kramer test ($P = 0.05$).

Results The transformation temperature was higher for each heat treatment condition compared with the control. Two clear thermal peaks were observed for the heat treatment at 440 °C. The specimen heated at 440 °C for 30 min exhibited the highest temperatures for M_s and A_f, with subsequently lower temperatures observed for specimens heated at 440 °C for 10 min, 500 °C for 30 min, 500 °C for 10 min, and control specimens. The sample heated at 440 °C for 30 min had the lowest bending load values ($P < 0.05$), both in the elastic range (0.5 mm deflection) and in the super-elastic range (2.0 mm deflection). The influence of heat treatment time was less than that of heat treatment temperature.

Conclusions Change in the transformation behaviour by heat treatment may be effective in increasing the flexibility of nickel–titanium endodontic instruments.

Keywords: bending property, differential scanning calorimetry, heat treatment, nickel–titanium alloy, phase transformation.

Received 24 December 2008; accepted 29 January 2009

Introduction

Nickel–titanium alloy has special properties, such as a low elastic modulus, high corrosion resistance, super-elasticity and shape memory, which have been applied widely in the dental field (Miura *et al.* 1986, Khier *et al.* 1991, Zhou *et al.* 2004). Super-elasticity and the shape memory effect are characterized by thermo-elastic martensitic transformation. At a temperature higher than the transformation temperature range, nickel–titanium alloy consists of the austenitic phase based on a B2 body-centred cubic crystal lattice, and in the lower temperature range, it consists of the martensitic phase, which is based on a monoclinic crystal lattice (Huang *et al.* 2003). The phase transformation behaviour of

Correspondence: Dr Yoshio Yahata, Pulp Biology and Endodontics, Department of Restorative Sciences, Graduate School, Tokyo Medical and Dental University, 5-45 Yushima 1-chome, Bunkyo-ku, Tokyo 113-8549, Japan (Tel.: +81 3 5803 5494; fax: +81 3 5803 5494; e-mail: y.yahata.endo@tmd.ac.jp).

nickel–titanium alloy is very sensitive to atomic composition, heat-treatment, manufacturing processes and additional factors (Miyazaki *et al.* 1982, Thompson 2000).

Walia *et al.* (1988) introduced nickel–titanium instruments to the field of endodontics because the increased flexibility over traditional stainless-steel instruments facilitates instrumentation in curved canals and enables efficient root canal preparation. Today, nickel–titanium endodontic instruments have assumed an important role in clinical endodontic treatment. A number of studies regarding the mechanical and metallurgical properties of nickel–titanium endodontic instruments have been reported. Schäfer *et al.* (2003)determined that the chemical composition of nickel–titanium endodontic instruments was based on 55-nitinol using X-ray energy-dispersive spectroscopy. However, X-ray energy-dispersive spectroscopy may not detect slight changes in the chemical composition of the alloy. Chemical composition shifts from stoichiometry have a significant effect on the characteristics of nickel–titanium alloy. In particular, the transformation temperature is extremely sensitive to composition. A 1% shift in the Ni content results in a 100 °C change in the martensitic transformation starting point or the reverse transformation finishing point (Otsuka & Wayman 1998). The design of the cross-sectional shape is also an important factor that directly affects the torsional and bending properties of nickel–titanium endodontic instruments (Turpin *et al.* 2000, Berutti *et al.* 2003, Schäfer *et al.* 2003). Heat treatment during manufacturing releases the internal strain caused by work-hardening and changes the phase transformation behaviour of nickel–titanium endodontic instruments (Kuhn *et al.* 2001, Kuhn & Jordan 2002, Hayashi *et al.* 2007). Miyai *et al.* (2006) reported that the bending properties of commercially available instruments were closely related to the transformation behaviour of the alloy.

It is known that the phase transformation behaviour affects the mechanical properties of nickel–titanium alloy (Yoneyama *et al.* 1993, 2002, Huang & Liu 2001). However, the relationship between bending properties and the phase transformation of nickel–titanium endodontic instruments has not been investigated clearly. Furthermore, there is little information available on the effect of heat treatment on nickel–titanium endodontic instruments.

The aim of this study was to investigate the effect of heat treatment on the bending properties of nickel–titanium endodontic instruments fabricated from nickel–titanium alloy wires in relation to their transformation behaviour.

Materials and methods

Specimens

Nickel–titanium alloy wire (1.00 mm diameter Ti-50.85 mol% Ni, NT-E4, Furukawa Techno Material, Kanagawa, Japan) with super-elasticity and a memorized straight shape was used. Conical specimens with a 0.30 mm tip diameter and 0.06 taper, as shown in Fig. 1, were fabricated using the wire.

Heat treatment condition

A total of 50 specimens were randomly assigned to five groups for heat treatment at 440 or 500 °C for a period of 10 or 30 min, as indicated in Table 1. Heat treatment was performed in a nitrate bath (AS-140 nitric acid salt, Parker Netsushori Kogyo Co., Ltd. Tokyo, Japan). After the heat treatment, each specimen was immediately quenched in water. Five specimens from each group were subjected to the following tests.

Differential scanning calorimetry (DSC)

The thermal behaviour associated with the phase transformation of the nickel–titanium alloy specimens was measured by DSC using 20 mg samples from the conical part of the specimens. Specifically, the samples were cut into four segments, sealed in aluminium cells, and then placed into the measuring chamber of a differential scanning calorimeter (DSC-7000; Ulvac, Tokyo, Japan). The chamber was filled with argon gas, and alpha alumina powder was used as the reference material. The temperature was increased from ambient

Figure 1 Photograph of a nickel–titanium alloy specimen before heat treatment.

Table 1 Heat treatment conditions for all specimen groups

Group	Heat treatment temperature (°C)	Heat treatment period (min)
440-10	440	10
440-30	440	30
500-10	500	10
500-30	500	30
Control	As received	

temperature to 100 °C, and subsequently the specimens were cooled to −100 °C and differences in energy were measured during the cooling process. Liquid nitrogen was used as a coolant. The specimen temperature was increased to 100 °C again to measure the energy required in the heating process. The heating rate was 0.17 °C/s.

The transformation temperatures were obtained from the intersection between extrapolations of the baseline and maximum gradient line of the lambda-type DSC curve. The martensitic transformation starting (M_s) and finishing (M_f) points and the reverse transformation starting (A_s) and finishing (A_f) points were determined.

Bending test

To evaluate the changes in the specimen flexibility caused by heat treatment, a cantilever-bending test apparatus designed by Miyai *et al.* (2006) was used. The specimen was first mounted on a movable stage, and the temperature of the specimen and apparatus was kept at 37 °C. The distance between the clamp edge and specimen tip was 9.5 mm, and the initial loading point was 3.0 mm from the tip. The specimen was loaded (1.0 mm/min) until the deflection reached 3.0 mm and then unloaded. The bending loads at deflections of 0.5 mm and 2.0 mm in the loading process were used for evaluation.

Data analysis

For the evaluation of the transformation temperatures and the bending load values, ANOVA was used for detection of the differences amongst the different heat-treatment groups. Differences between the groups were detected using the Tukey–Kramer's *post hoc* test, and the statistical significance was set at $P = 0.05$.

Results

DSC measurement

Figure 2 shows typical DSC curves obtained for each heat treatment group. The upper peak indicates the exothermic reaction accompanying the martensitic transformation from the austenitic phase during the cooling process, whilst the lower peak indicates the endothermic reaction caused by the reverse transformation during the heating process. Compared with the case for the untreated control specimen, the thermal peaks were at higher temperature for all heat treatment groups. For the specimen heated at 440 °C for 10 min (denoted 440-10) and the 440-30 specimen, two thermal peaks were clearly observed during the heating process.

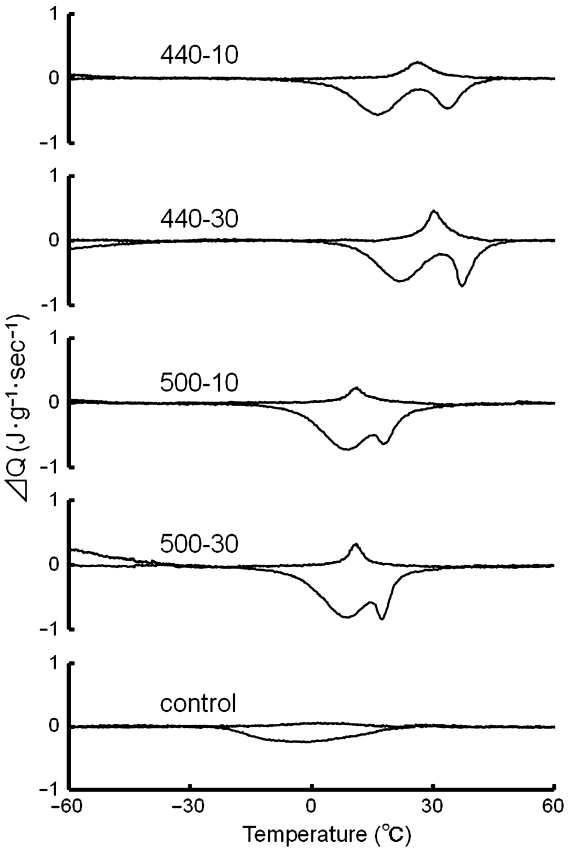

Figure 2 Typical DSC curves for specimens heat-treated at 440 °C for 10 min, 440 °C for 30 min, 500 °C for 10 min, 500 °C for 30 min, and a control specimen.

The transformation temperatures of all specimen groups are given in Table 2. The highest temperatures for M_s and A_f were recognized for the 440-30 specimen, with subsequently lower temperatures for the 440-10, 500-30, 500-10 and control specimens. M_s and A_f for the 440-10 and 440-30 specimens were significantly higher ($P < 0.05$) than those for 500-10, 500-30 and the control specimens. A_f for the 440-10 and 440-30 specimens exceeded 37 °C. For A_s and M_f, statistically significant differences were recognized in all the groups.

Bending test

Typical load-deflection curves for each heat-treated group and the control, indicating super-elastic

Table 2 Phase transformation temperatures for each specimen group (mean ± SD, $n = 5$ for all conditions)

Group	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)
440-10	34.6 ± 1.3[a]	20.6 ± 0.6[a]	3.3 ± 2.0[a]	38.0 ± 5.1[a,c]
440-30	35.1 ± 0.9[a]	26.0 ± 0.5[b]	7.7 ± 1.0[b]	42.4 ± 0.6[a]
500-10	18.4 ± 3.2[b]	6.9 ± 0.6[c]	−3.9 ± 1.2[c]	25.4 ± 2.6[b]
500-30	22.2 ± 0.6[c]	16.3 ± 0.5[d]	11.4 ± 1.1[d]	33.0 ± 2.4[c]
control	17.4 ± 0.7[b]	−16.9 ± 1.7[e]	−22.0 ± 1.3[e]	25.7 ± 1.6[b]

Values with same superscript letters are not significantly different ($P > 0.05$)

behaviour, are shown in Fig. 3. On the application of stress, the initial portion of the load-deflection curve shows a linear relationship due to elastic deformation. Above this range, the load level becomes almost constant owing to the stress-induced martensitic transformation. During the unloading process, the load is decreased rapidly and becomes constant owing to the reverse transformation. Subsequently, elastic unloading occurs with a small permanent residual deflection.

Table 3 shows bending loads at deflection of 0.5 mm and 2.0 mm deflection, corresponding to the elastic range and super-elastic range respectively. In elastic range, the 440-30 specimens showed the minimum bending load values within this range. Both the 440-10 and 440-30 specimens revealed significantly lower

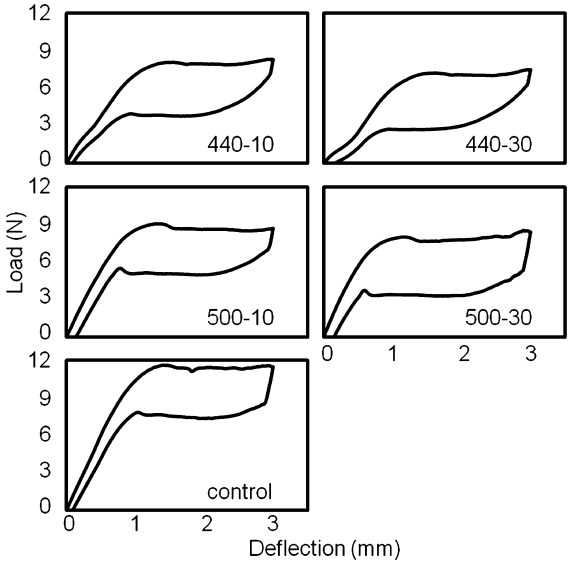

Figure 3 Typical load deflection curves for specimens heat-treated at 440 °C for 10 min, 440 °C for 30 min, 500°C for 10 min, 500 °C for 30 min, and a control specimen.

Table 3 Bending load values at deflections of 0.5 mm and 2.0 mm for each specimen groups (mean ± SD, $n = 5$ for all conditions)

Group	0.5 mm deflection (N)	2.0 mm deflection (N)
440-10	3.69 ± 0.18[a]	8.18 ± 0.32[a,b]
440-30	3.01 ± 0.37[b]	7.37 ± 0.43[b]
500-10	5.67 ± 0.23[c]	8.69 ± 0.39[a]
500-30	5.40 ± 0.34[c]	7.62 ± 0.46[b]
control	5.61 ± 0.27[c]	10.98 ± 0.48[c]

Values with same superscript letters are not significantly different ($P > 0.05$)

bending load values than the 500-10, 500-30 and control specimens did ($P < 0.05$). In super-elastic range, the 440-30 specimens also showed the minimum bending load value, whilst the control specimens exhibited the highest bending load value of all the groups ($P < 0.05$).

Discussion

Transformation behaviour

Super-elasticity and the shape-memory of nickel–titanium alloy are derived from the thermo-elastic martensitic transformation, and thermal changes are recognized owing to the differences in the free energies between the austenitic and martensitic phases. DSC provides a microcalorimetric determination of the reference material and specimen. The measurements are reproducible and generally used to determine the transformation behaviour of nickel–titanium alloy (Bradley *et al.* 1996, Brantley *et al.* 2002, American Society of Testing and Materials 2005). Some previous studies suggested that heat treatment is an important procedure that can be used to manifest the original mechanical properties of nickel–titanium alloy by releasing crystal lattice defects and contributing to changes in the phase transformation behaviour (Kuhn *et al.* 2001, Kuhn & Jordan 2002, Hayashi *et al.* 2007). The heat treatment conditions used were based on a previous study (Yoneyama *et al.* 2002). The influence of heat treatment temperature below 300 °C is not sufficient to release crystal lattice defects. On the other hand, re-crystallization occurs above 600 °C and thus super-elasticity and shape memory are incomplete in this range. Therefore, heat treatment is usually performed at an appropriate temperature between 300 and 600 °C, releasing crystal lattice defects so as to diminish the internal strain energy (Miyazaki & Otsuka 1989).

From the DSC measurements, A_f for 440-10 and 440-30 specimens exceeded 37 °C, the assumed temperature in an oral environment. Therefore, the alloy after these treatments consisted of a mixed phase containing both the austenitic and martensitic phases. In addition, two clear endothermic peaks were observed during the heating of the 440-10 and 440-30 specimens. This indicates that the reverse transformation of these alloys passes through the intermediate R-phase. The stress hysteresis for the intermediate R-phase transition is lower than that of the martensitic transition (Miyazaki & Otsuka 1986), and the elastic modulus of this phase is lower than that of the martensitic phase (Kuhn & Jordan 2002). M_s and A_f were lower than 37 °C for the 500-10, 500-30 and control specimens, confirming that these alloys consist mainly of the austenitic phase.

With respect to the heat treatment period, longer heat treatment tended to increase the transformation temperatures.

Bending properties

The mechanical properties of nickel–titanium endodontic instruments are known to be controlled by cold working and heat treatment during manufacturing (Kuhn *et al.* 2001).

The 0.5 mm deflection bending load corresponds to the elastic range and depends on the elastic modulus of the specimen. The elastic modulus of nickel–titanium alloy varies depending on the constituent phases; that of the martensitic phase is lower than that of the austenitic phase, and it changes significantly in the vicinity of the transformation temperature range. The transformation temperatures obtained suggest that at the temperature of an oral environment, the 440-10 and 440-30 specimens consist of a mixed phase and the 500-10, 500-30 and control specimens consist of the austenitic phase. This difference in the constituent phases is thought to be one of the reasons for the low elastic modulus of the 440-10 and 440-30 specimens compared with the moduli for 500-10, 500-30 and control specimens.

For the 2.0 mm deflection, which corresponds to the super-elastic load range, the bending loads for all heat treatment groups were lower than that of the control. The super-elasticity of nickel–titanium alloy is based on the stress-induced martensitic transformation, which causes twin deformation. The bending load in the super-elastic range is dependent on the critical stress required to induce martensitic transformation, and can be explained by the Clausius–Clapeyron relationship at a temperature higher than M_s, expressed as

$$d\sigma/dT = \Delta S^{p \to m}/\Delta \varepsilon^{p \to m}$$

where $\Delta S^{p \to m}$ is the entropy of transformation per unit volume, $\Delta \varepsilon^{p \to m}$ is the strain in the transformation, σ is stress and T is temperature. $\Delta S^{p \to m}$ and $\Delta \varepsilon^{p \to m}$ are defined by the alloy material and take constant values (Otsuka & Wayman 1998). Therefore, a linear relationship exists between the stress and temperature; the martensitic transformation stress increases with increasing testing temperature or decreasing M_s. The austenitic phase is more stable at high temperature and a high stress is required for stress-induced martensitic transformation. From this relationship, M_s values for the 440-10 and 440-30 specimens were more than 15 °C higher than that for the control, and the critical stress for inducing martensitic transformation was reduced.

For the 500-10 and 500-30 specimens, the bending load values in the super-elastic range were less than that for the control. After reaching the critical stress for inducing martensitic transformation, complete martensitic transformation requires lower stress because the internal strain is released by heat treatment.

The bending load values at 0.5 mm and 2.0 mm for the 30 min-treated specimens were less than values for the 10 min-treated specimens. This suggests that the treatment period may affect the increase in transformation temperatures.

It was clarified that the bending properties of nickel–titanium endodontic instruments were closely related not only to the cross-sectional shape but also to the transformation behaviour. However, increasing flexibility and/or consisting of a mixed phase of austenitic and martensitic phase may affect to other important clinical properties such as fracture resistance and cutting efficiency. Further study needed to investigate the effect of heat treatment on other clinical factors of nickel-titanium endodontic instruments.

Conclusions

The effect of heat treatment on the transformation behaviour and bending properties of nickel–titanium endodontic instruments was investigated by DSC and in a cantilever-bending test. The following conclusions were obtained.

1. The transformation temperature was increased by heat treatment, and the increase in the transformation temperature was related to the heat treatment temperature.

2. Two clear peaks were recognized for the 440-10 and 440-30 specimens during the heating, suggesting that the two steps of transformation pass through the intermediate R-phase.

3. In the elastic and super-elastic ranges, the 440-30 specimens displayed the minimum bending load values. The bending properties of nickel–titanium endodontic instruments may be closely related with the transformation behaviour in the crystal lattice structure.

4. The flexibility in the elastic range is influenced by M_s and A_f. Nickel–titanium endodontic instruments with high transformation temperatures may exhibit lower bending loads than those with low transformation temperatures do.

The change in the transformation behaviour with heat treatment may have a significant effect on the mechanical properties of nickel–titanium endodontic instruments. Under the experimental conditions examined, the heat-treatment of nickel–titanium endodontic instruments at 440 °C may be effective in increasing their flexibility.

References

American Society of Testing and Materials (2005) *Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis*, USA: ASTM.

Berutti E, Chiandussi G, Gaviglio I, Ibba A (2003) Comparative analysis of torsional and bending stresses in two mathematical models of nickel-titanium rotary instruments: ProTaper versus ProFile. *Journal of Endodontics* **29**, 15–9.

Bradley TG, Brantley WA, Culbertson BM (1996) Differential scanning calorimetry (DSC) analyses of superelastic and non superelastic nickel-titanium orthodontic wires. *American Journal of Orthodontics and Dentofacial Orthopedics* **109**, 589–97.

Brantley WA, Svec TA, Iijima M, Powers JM, Grentzer TH (2002) Differential scanning calorimetric studies of nickel titanium endodontic instruments. *Journal of Endodontics* **28**, 567–72.

Hayashi Y, Yoneyama T, Yahata Y *et al.* (2007) Phase transformation behaviour and bending properties of hybrid nickel-titanium rotary endodontic instruments. *International Endodontic Journal* **40**, 247–53.

Huang X, Liu Y (2001) Effect of annealing on the transformation behavior and superelasticity of NiTi shape memory alloy. *Scripta Materialia* **45**, 153–60.

Huang X, Ackland GJ, Rabe KM (2003) Crystal structures and shape-memory behaviour of NiTi. *Nature Materials* **2**, 307–11.

Khier SE, Brantley WA, Fournelle RA (1991) Bending properties of superelastic and non superelastic nickel-titanium orthodontic wires. *American Journal of Orthodontics and Dentofacial Orthopedics* **99**, 310–8.

Kuhn G, Jordan L (2002) Fatigue and mechanical properties of nickel-titanium endodontic instruments. *Journal of Endodontics* **28**, 716–20.

Kuhn G, Tavernier B, Jordan L (2001) Influence of structure on nickel-titanium endodontic instruments failure. *Journal of Endodontics* **27**, 516–20.

Miura F, Mogi M, Ohura Y, Hamanaka H (1986) The super-elastic property of the Japanese NiTi alloy wire for use in orthodontics. *American Journal of Orthodontics and Dentofacial Orthopedics* **90**, 1–10.

Miyai K, Hayashi Y, Ebihara A, Doi H, Suda H, Yoneyama T (2006) Influence of phase transformation on the torsional and bending properties of nickel-titanium rotary endodontic instruments. *International Endodontic Journal* **39**, 119–26.

Miyazaki S, Otsuka K (1986) Deformation and transition behavior associated with the *R*-phase in Ti-Ni alloys. *Metallurgical and Materials Transactions A* **17**, 53–63.

Miyazaki S, Otsuka K (1989) Development of shape memory alloys. *ISIJ International* **29**, 353–77.

Miyazaki S, Ohmi Y, Otsuka K, Suzuki Y (1982) Characteristics of deformation and transformation pseudoelasticity in NiTi alloys. *Journal de Physique Colloques* **43**, C4–255.

Otsuka K, Wayman CM (1998) *Shape Memory Alloys*, 1st edn. Cambridge, UK: Cambridge University Press.

Schäfer E, Dzepina A, Danesh G (2003) Bending properties of rotary nickel-titanium instruments. *Oral Surgery, Oral Medicine, Oral Pathology, Oral Radiology and Endodontics* **96**, 757–63.

Thompson SA (2000) An overview of nickel-titanium alloys used in dentistry. *International Endodontic Journal* **33**, 297–310.

Turpin YL, Chagneau F, Vulcain JM (2000) Impact of two theoretical cross-sections on torsional and bending stresses of nickel-titanium root canal instrument models. *Journal of Endodontics* **26**, 414–7.

Walia H, Brantley WA, Gerstein H (1988) An initial investigation of the bending and torsional properties of nitinol root canal files. *Journal of Endodontics* **14**, 346–51.

Yoneyama T, Doi H, Hamanaka H (1993) Bending properties and transformation temperatures of heat treated Ni-Ti alloy wire for orthodontic appliances. *Journal of Biomedical Materials Research* **27**, 399–402.

Yoneyama T, Doi H, Kobayashi E, Hamanaka H (2002) Effect of heat treatment with the mould on the super-elastic property of Ti-Ni alloy castings for dental application. *Journal of Materials Sciences Materials in Medicine* **13**, 947–51.

Zhou HZ, Hu M, Yao J, Ma L (2004) Rapid lengthening of rabbit mandibular ramus by using nitinol spring: a preliminary study. *The Journal of Craniofacial Surgery* **15**, 725–9.