ELSEVIER

Thermochimica Acta 392–393 (2002) 329–337

thermochimica acta

www.elsevier.com/locate/tca

Temperature-modulated DSC study of phase transformations in nickel–titanium orthodontic wires

W.A. Brantley[a,*], M. Iijima[a,b], T.H. Grentzer[c]

[a]*College of Dentistry, Ohio State University, 305 West 12th Avenue, Mailbox 191, P.O. Box 182357, Columbus, OH 43218-2357, USA*

[b]*School of Dentistry, Health Sciences University of Hokkaido, Ishikari-Tobetsu, Japan*

[c]*Ashland Specialty Chemical Company, Dublin, OH 43017, USA*

Abstract

Nickel–titanium archwire alloys are very important for clinical orthodontics because of their wide elastic range and excellent springback, along with their ability to deliver highly desirable light forces for tooth movement. Recently, nickel–titanium orthodontic alloys have been developed that possess shape memory over the temperature range of the oral environment, and these archwires have considerable promise for the clinical treatment of patients. The shape memory is associated with a reversible transformation from martensitic NiTi to austenitic NiTi that is completed at mouth temperature. While extensive conventional differential scanning calorimetry (DSC) studies have been performed on commercial nickel–titanium orthodontic wire alloys to characterize their phase transformation behavior, the present study is the first time that temperature-modulated DSC (TMDSC) has been used for this purpose. Two commercial nickel–titanium wires possessing shape memory were analyzed, along with a third commercial nickel–titanium wire lacking shape memory. The TMDSC analyses were generally performed from −130 to 100 °C for both the heating and cooling cycles, since there can be differences in the processes and the temperature ranges for the forward and reverse transformations. Improved resolution of the phase transformations was achieved with the use of TMDSC, compared to conventional DSC, and the novel results indicate the complexity of the phase transformation processes.

Keywords: Thermal analysis; Temperature-modulated differential scanning calorimetry; Phase transformation; Nickel–titanium alloys; Shape memory; Orthodontics; Archwires

1. Introduction

The potential of nickel–titanium wires for orthodontics was first reported by Andreasen and his colleagues [1,2], and the first commercial nickel–titanium archwire (Nitinol) was subsequently introduced by the Unitek Corporation (now 3M Unitek). This wire alloy became popular because of its wide elastic range and excellent springback, and because of its much lower modulus of elasticity [3], compared to the wrought stainless steel and cobalt–chromium–nickel alloys in use at the time, which resulted in substantially lighter forces for tooth movement.

Subsequently, nickel–titanium orthodontic wire alloys [4,5] possessing superelastic behavior [6,7] (frequently termed *pseudoelastic* [8] in the materials science literature) were developed. In the early 1990's, nickel–titanium wire alloys for orthodontics with true

* Corresponding author. Tel.: +1-614-292-0773; fax: +1-614-292-9422.
E-mail address: brantley.1@osu.edu (W.A. Brantley).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00119-3

shape memory at the temperatures of the oral environment [9,10] were marketed. Currently, a wide variety of nickel–titanium orthodontic wire alloys are available, which may be classified as nonsuperelastic, superelastic (without shape memory), and shape memory.

It is well-known that the shape memory behavior of the nickel–titanium alloys, whose composition is close to the equiatomic ratio of nickel and titanium, is associated with a reversible transformation between the low-temperature martensitic NiTi phase and the high-temperature austenitic NiTi phase, which occurs by a twinning mechanism [7]. An additional phase, termed the R-phase, is sometimes observed as an intermediate step for the transformation between martensitic NiTi and austenitic NiTi [11]. The temperature dependence of the phase transformation behavior, which determines whether a given nickel–titanium orthodontic alloy is nonsuperelastic, superelastic or shape memory, is readily studied by conventional differential scanning calorimetry (DSC) [12,13], which has also been used in the engineering materials science investigations of these alloys [14]. While X-ray diffraction analyses of the nickel–titanium orthodontic wires provide very useful information about the presence of the martensitic and austenitic NiTi phases [15], this technique only examines the sample volume within less than about 50 μm of the surface, whereas DSC provides information about the bulk sample. Electrical resistivity measurements have also been employed to investigate the phase transformations in the nickel–titanium orthodontic wires [16], but this technique does not provide information about the enthalpy changes associated with the transformations.

The purpose of the present study was to use temperature-modulated DSC (TMDSC) to investigate the phase transformations in three representative commercial nickel–titanium orthodontic wires, which have been previously examined by conventional DSC [13,17]. It was hypothesized that the TMDSC analyses might provide greater resolution of the complex phase transformations occurring in these alloys.

2. Experimental

The three nickel–titanium orthodontic wires selected for study were Sentalloy Yellow (Tomy International, Tokyo, Japan), Neo Sentalloy (GAC International, Islandia, NY, USA), and Nitinol (3M Unitek, Monrovia, CA, USA). The cross-section dimensions of the wires were 0.016 in. × 0.022 in. (Sentalloy and Neo Sentalloy) and 0.019 in. × 0.025 in. (Nitinol); both sizes are popular for clinical orthodontics. The wires were carefully cut with a water-cooled, slow-speed diamond saw to minimize mechanical stresses that might change the proportions of the austenitic and martensitic NiTi phases from those in the as-received wires. Each test sample consisted of five or six 5 mm segments placed in an open aluminum pan; no crimped top was used to avoid mechanical stresses on the wires. Two samples each of Sentalloy and Neo Sentalloy, and three samples of Nitinol, were analyzed.

The TMDSC analyses were conducted (Model 2910 DSC, TA Instruments, Wilmington, DE, USA) over a temperature range from −130 to 100 °C, after analysis of the first Sentalloy sample revealed that no phase transformation occurred with a lower starting temperature of −150 °C. For each analysis the sample was first heated from −130 to 100 °C and then subsequently cooled from 100 °C back to −130 °C. The linear heating or cooling rate was 2 °C/min, and the oscillation amplitude was 0.318 °C with a period of 60 s. These modulation conditions provided heating-only conditions during the heating cycle and cooling-only conditions during the cooling cycle. During each analysis the DSC cell was purged with dry helium at a rate of 25 cm^3/min through the purge port and 100 cm^3/min through the vacuum port in order to maintain a moisture-free test environment. Temperature calibration of the TMDSC apparatus was performed with *n*-pentane, deionized water and indium.

3. Results

3.1. Sentalloy orthodontic wire

The TMDSC heating results for one Sentalloy sample in Fig. 1 reveal two overlapping endothermic peaks on the reversing heat flow curve with a combined area of $\Delta H \approx 16$ J/g. These peaks correspond to transformation from martensitic NiTi to R-phase followed by transformation at higher temperature (peak at about 21 °C) from R-phase to austenitic NiTi [12–14]. On the nonreversing heat flow curve these two phase transformations are represented by an exothermic peak at

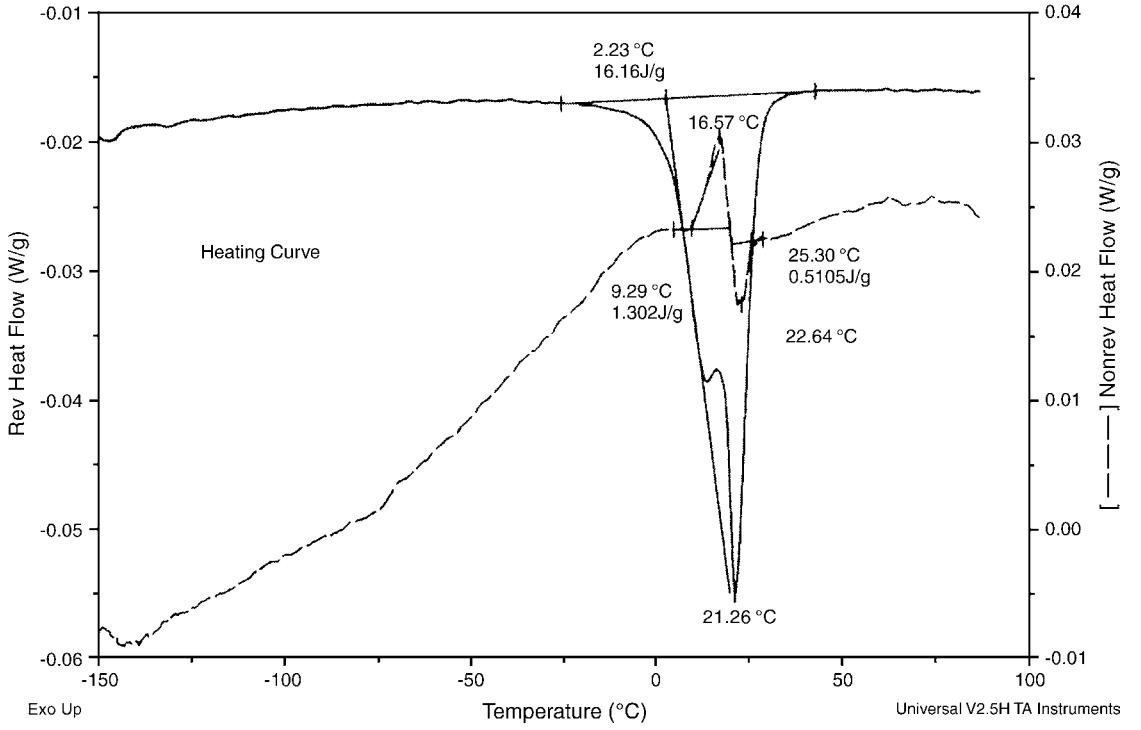

Fig. 1. TMDSC heating results for a Sentalloy test sample. The reversing heat flow curve (top) has a horizontal baseline.

about 17 °C ($\Delta H = 1.3$ J/g) followed by an endothermic peak at about 23 °C ($\Delta H = 0.5$ J/g). Although similar results were observed on the nonreversing heat flow curve during the heating cycle of the other Sentalloy sample, these peaks lacked the distinctive appearance shown in Fig. 1. An offset (slope change) at about −70 °C was also found on the nonreversing heat flow curve; a similar offset occurred near −85 °C for the other Sentalloy sample. Fig. 1 shows [13] that Sentalloy exhibits shape memory in the oral environment, since the austenite-finish temperature (A_f), where the wire has transformed completely to the austenitic NiTi structure on heating, is less than 37 °C.

The TMDSC cooling results for the Sentalloy sample of Fig. 1 are presented in Fig. 2; similar cooling results were found for the other Sentalloy sample. There is an exothermic peak ($\Delta H = 6.4$ J/g) at about 19 °C on the reversing heat flow curve and two exothermic peaks on the nonreversing heat flow curve, where the much larger peak ($\Delta H = 10.9$ J/g) is located near −56 °C. This latter peak is assumed to correspond to the offset at about −70 °C in Fig. 1. Comparing this figure to the conventional DSC cooling curves for two shape memory alloys, Neo Sentalloy and Titanal LT (Lancer Orthodontics, San Marcos, CA, USA) [13] and to conventional DSC results obtained for Sentalloy [17], the peak on the reversing heat flow curve in Fig. 2 is attributed to transformation from austenitic NiTi to R-phase, and the larger peak on the nonreversing heat flow curve is attributed to transformation from R-phase to martensitic NiTi. The small exothermic peak on the nonreversing heat flow curve at about 19 °C is assumed to be associated with a portion of the transformation of austenitic NiTi to R-phase; this transformation principally has reversing character.

3.2. Neo Sentalloy orthodontic wire

The TMDSC heating results for Neo Sentalloy, which also exhibits shape memory [13], are shown in Fig. 3; similar results were found for both samples. The large endothermic peak ($\Delta H = 12.2$ J/g) at about 22 °C on the reversing heat flow curve corresponds to

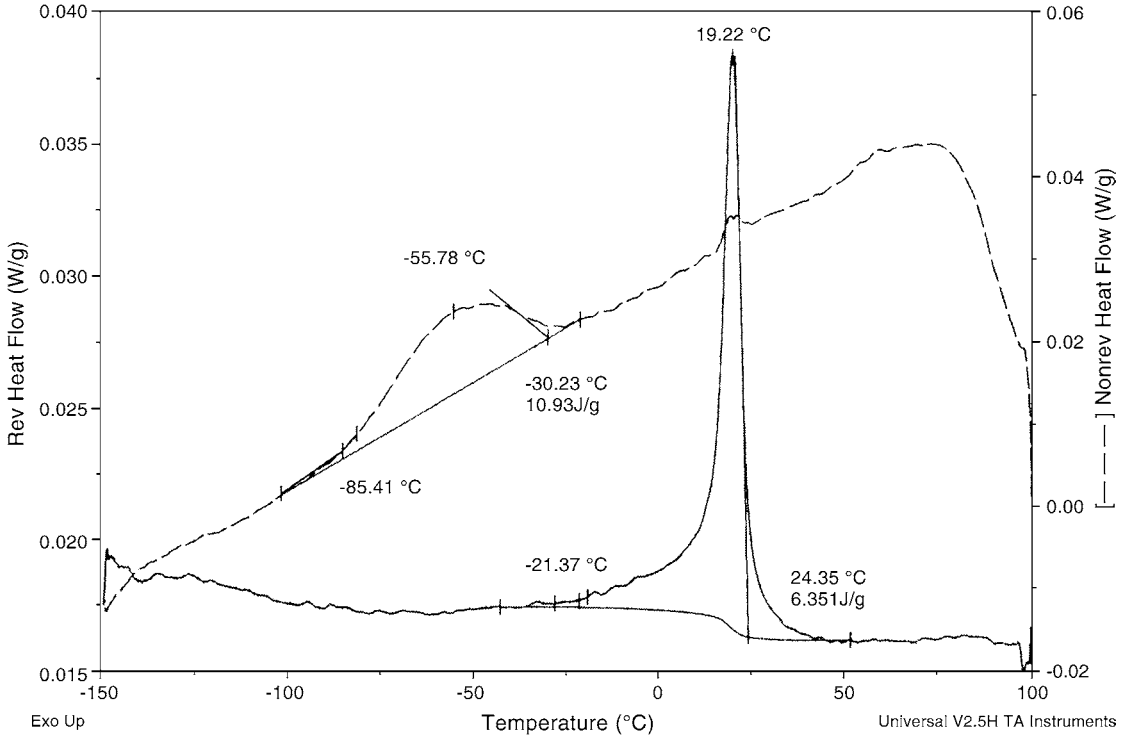

Fig. 2. TMDSC cooling results for the same Sentalloy test sample as in Fig. 1. The reversing heat flow curve (bottom) has a horizontal baseline.

the direct transformation from martensitic NiTi to austenitic NiTi without the intermediate R-phase, using the same interpretation as for the single endothermic peak previously found on the conventional DSC heating curve for Neo Sentalloy [13]. The endothermic peak temperature for the different test sample used in that earlier study was near 30 °C. The very small peak on the right shoulder near 35 °C in Fig. 3, not observed with conventional DSC [13], was also found on the reversing heat flow curve during the heating cycle of the other Neo Sentalloy sample.

However, the nonreversing heat flow curve in Fig. 3 contains two overlapping endothermic peaks that occur over approximately the same temperature range as the large endothermic peak on the reversing heat flow curve. Following the same interpretation used for Fig. 1, these two peaks are interpreted [12–14] as corresponding to the transformation from martensitic NiTi to R-phase, followed by the transformation from R-phase to austenitic NiTi with increasing temperature. Accordingly, TMDSC has provided greater resolution of this phase transformation process than that available with conventional DSC, where only a single peak was observed for this wire alloy [13]. A large exothermic peak ($\Delta H = 9.0$ J/g) on the nonreversing heat flow curve at about -74 °C, not found on the reversing heat flow curve or with conventional DSC [13], is attributed to some transformation in the martensitic NiTi structure [14].

The TMDSC cooling results for Neo Sentalloy are shown in Fig. 4, where again similar behavior was found for both samples. The exothermic peak ($\Delta H = 4.6$ J/g) at about 19 °C on the reversing heat flow curve is assumed to correspond to the transformation from austenitic NiTi to R-phase, based upon conventional DSC results where a large exothermic peak was observed [13] over a similar temperature range. The small peak ($\Delta H = 0.1$ J/g) at about -38 °C may correspond to some reversible transformation within the martensitic NiTi structure. On the nonreversing heat flow curve in Fig. 4, the relative peak areas for these transformations are reversed. The

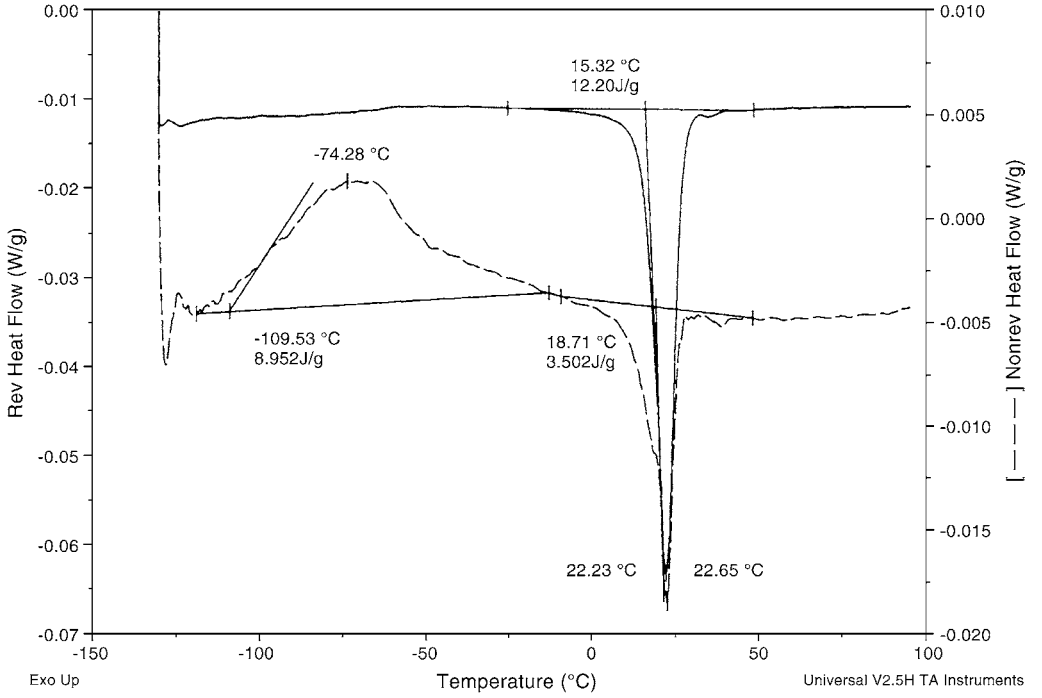

Fig. 3. TMDSC heating results for a Neo Sentalloy test sample. The reversing heat flow curve (top) has a horizontal baseline.

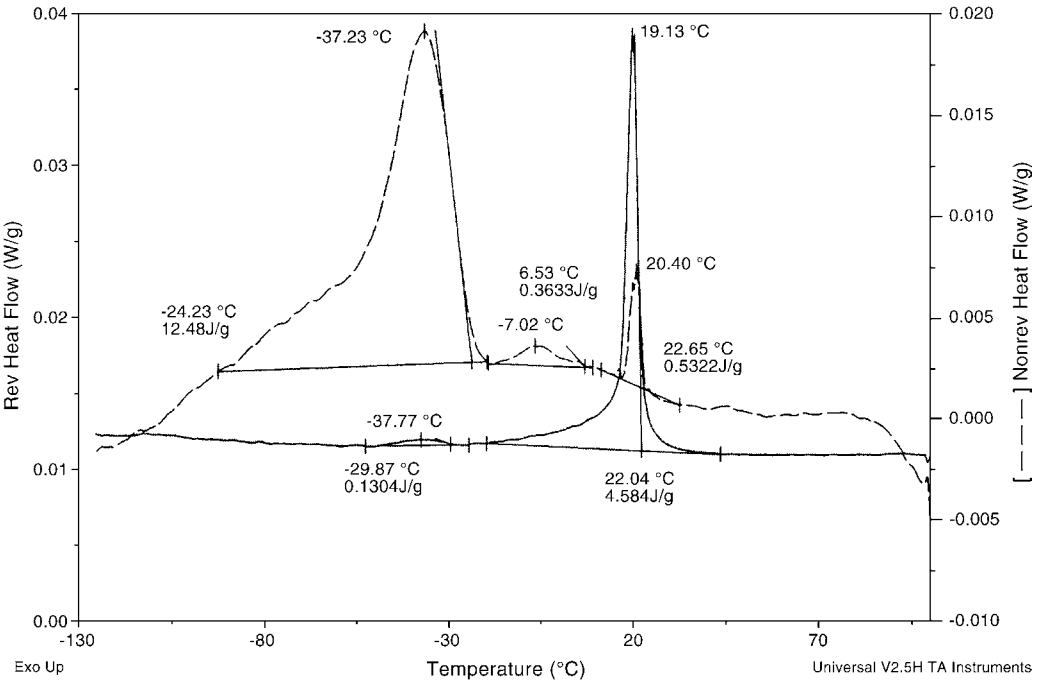

Fig. 4. TMDSC cooling results for the same Neo Sentalloy test sample as in Fig. 3. The reversing heat flow curve (bottom) has a horizontal baseline.

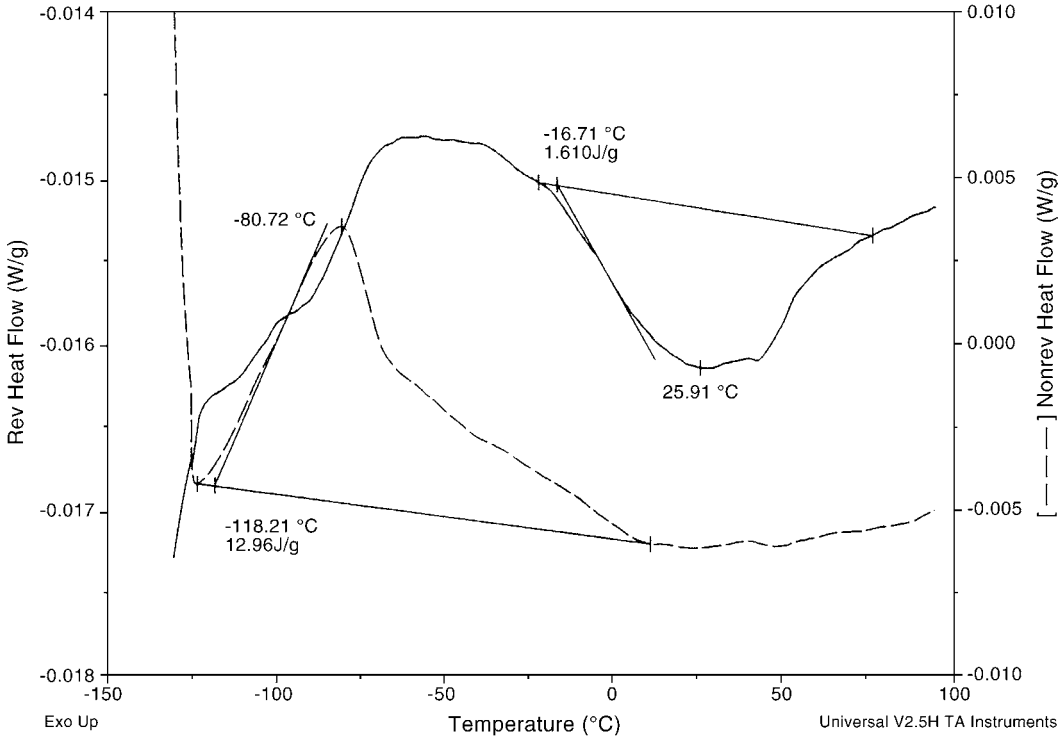

Fig. 5. TMDSC heating results for a Nitinol test sample. The reversing heat flow plot is the top curve (solid line).

enthalpy change ($\Delta H = 12.5$ J/g) for the transformation from R-phase to martensitic NiTi (peak at about -37 °C) is much larger than the enthalpy change ($\Delta H = 0.5$ J/g) for the transformation from austenitic NiTi to R-phase (peak at about 20 °C). This large peak, which contains an unresolved lower temperature left shoulder, may also be associated with transformations within the martensitic NiTi structure [14]. A small peak ($\Delta H = 0.4$ J/g) at about -7 °C on the nonreversing heat flow curve may represent initial transformation of R-phase to martensitic NiTi or perhaps final transformation of the remaining austenitic NiTi to R-phase.

3.3. Nitinol orthodontic wire

The TMDSC analyses of Nitinol were complicated by very small values for the reversible and nonreversible heat flows, as shown in Figs. 5 and 6 for the heating and cooling results, respectively. This behavior arises because relatively little phase transformation occurs in the nonsuperelastic orthodontic wire alloy, which is dominated by a largely stable, work-hardened martensitic NiTi structure [13]; Nitinol does not exhibit shape memory in the oral environment. As a consequence, the ordinarily horizontal baseline for the reversing heat flow curve, evident in Figs. 1–4, was not observed for the TMDSC heating and cooling curves of this alloy. (Note that more sensitive scales were used for the reversing heat flow curves in Figs. 5 and 6, compared to the scales used for the nonreversing heat flow curves in these two figures). Results similar to Figs. 5 and 6 were obtained for a second Nitinol sample. However, irregular reversing and nonreversing heating TMDSC curves were obtained for a third sample, presumably due to the loss of thermal contact between the individual wire segments.

For the heating TMDSC results in Fig. 5, a broad and shallow peak ($\Delta H = 1.6$ J/g) centered at about 26 °C on the reversing heat flow curve is interpreted as corresponding to the direct transformation from martensitic NiTi to austenitic NiTi [13]. At the temperature of the oral environment (37 °C), this wire alloy would be a mixture of martensitic NiTi and austenitic

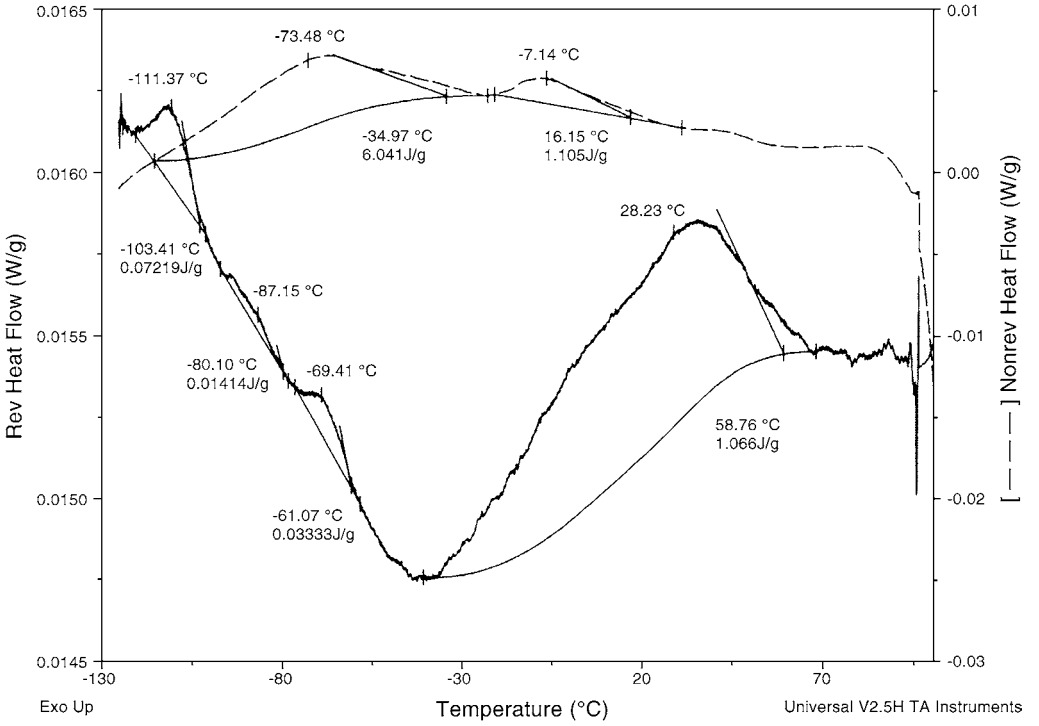

Fig. 6. TMDSC cooling results for the same Nitinol test sample as in Fig. 5. The reversing heat flow plot is the bottom curve (solid line).

NiTi, rather than the completely austenitic NiTi structure possessed by Sentalloy and Neo Sentalloy (Figs. 1–4). A large, broad peak ($\Delta H \approx 13$ J/g) at about -81 °C on the nonreversing heat flow curve is assumed to arise from phase transformation within the complex martensitic NiTi structure of this alloy [14]. No peak over this temperature range was previously observed with conventional DSC analysis of this alloy [13].

The cooling TMDSC results in Fig. 6 reveal a broad and shallow peak ($\Delta H \approx 1$ J/g) on the reversing heat flow curve, centered at about 30 °C, which is assumed to represent the direct transformation from austenitic NiTi to martensitic NiTi by analogy with Fig. 5. Three very weak peaks (ΔH ranging from 0.01 to 0.07 J/g), centered at about -70, -90 and -110 °C, are attributed to unknown low-temperature phase transformations in the martensitic NiTi [14], further demonstrating the complexity of this structure in the Nitinol alloy. Broad peaks centered at about -10 °C ($\Delta H \approx 1$ J/g) and -70 °C ($\Delta H \approx 6$ J/g) on the nonreversing heat flow curve are correspondingly attributed to transformation from austenitic NiTi to martensitic NiTi, followed by phase transformation within the martensitic NiTi structure.

4. Discussion

The interpretation of the present TMDSC plots follows from the peak assignments in previous publications of the DSC analyses of nickel–titanium orthodontic wires [12,13]. In the present experimental procedure, when each test sample was cooled to approximately -150 °C before beginning the initial TMDSC heating cycle (Figs. 1, 3 and 5), the orthodontic wires were converted to the martensitic NiTi structure. At the end of this heating cycle (100 °C), the wires were transformed to the austenitic NiTi structure, which was the starting condition for the test samples with the cooling TMDSC curves in Figs. 2, 4 and 6.

Comparison of the present TMDSC results for Neo Sentalloy (Figs. 3 and 4) and Nitinol (Figs. 5 and 6)

with those previously obtained by conventional DSC [13] illustrates that much higher resolution and more information about the phase transformations in these nickel–titanium orthodontic alloys is obtained with TMDSC. A similar conclusion was evident when unpublished recent DSC analyses of Sentalloy [17] were compared with the TMDSC results in Figs. 1 and 2. (It is important to note that a more sensitive scale has been used for the reversing heat flow curve in Fig. 2, compared to the scale for the nonreversing heat flow curve. This situation is reversed in Figs. 3 and 4, where a more sensitive scale was used for the nonreversing heat flow curve compared to the scale used for the reversing heat flow curve). The present enthalpy changes for the overall transformation between martensitic NiTi and austenitic NiTi lie within the range of values (∼1–20 J/g) previously obtained by conventional DSC for a variety of nickel–titanium orthodontic wires [12,13].

A noteworthy feature for the Neo Sentalloy (Fig. 3) and Nitinol (Figs. 5 and 6) orthodontic wires analyzed in this study is the apparent occurrence of low-temperature phase transformations within the martensitic NiTi structure [14]. As previously explained, conventional DSC analysis of Sentalloy [17] indicates that the low-temperature peak at about −55 °C on the nonreversing heat flow curve during the cooling cycle is associated with the transformation from R-phase to martensitic NiTi, rather than to transformation within the martensitic NiTi structure.

Further research will be needed to elucidate this highly complex martensitic NiTi structure [14] in these orthodontic wires, where substantial mechanical deformation with intermediate heat treatments is employed during the proprietary manufacturing sequence [10]. The present results indicate that the low-temperature phase transformations involving the martensitic NiTi structure typically have nonreversing character and occur over a relatively wide temperature range. The TMDSC analyses have shown that all of the phase transformations (involving austenitic NiTi and R-phase, as well as martensitic NiTi) in these wires can have both reversing and nonreversing character.

Future TMDSC studies are necessary to examine whether the phase transformations in these nickel–titanium orthodontic alloys are significantly affected by different linear heating/cooling rates and modulation conditions, and by repeated heating and cooling cycles, as well as to determine the nature of several presently unknown peaks. Such studies must be complemented by fundamental materials science research to gain further insight into the atomistic mechanisms for these phase transformations and to elucidate the origins of the reversing and nonreversing behavior.

5. Conclusions

TMDSC has provided greater resolution of the heating and cooling curves for nickel–titanium orthodontic wires than is possible with conventional DSC, along with potentially greater insight into the fundamental nature of the phase transformation processes. The two shape memory nickel–titanium wires investigated have the transformation to the austenitic NiTi structure completed at the temperature of the oral environment, whereas transformation is completed substantially above this temperature for the third nickel–titanium wire that did not possess shape memory. It was found that transformations in the shape memory wires between martensitic NiTi and austenitic NiTi, or between R-phase and austenitic NiTi, had both reversing and nonreversing character. A notable observation is the apparent occurrence of low-temperature phase transformations in the martensitic NiTi structures of two wire products studied. However, additional research with different linear heating/cooling rates and modulation conditions, and with repeated heating and cooling cycles, will be required to determine whether the character and kinetics of these phase transformations will be significantly affected.

Acknowledgements

The authors thank the manufacturers for contributing the orthodontic wires used in this study and Dr. John C. Mitchell for use of his laboratory facilities to prepare the wire segments for the test samples.

References

[1] G.F. Andreasen, T.B. Hilleman, J. Am. Dental Assoc. 82 (1971) 1373.
[2] G.F. Andreasen, P.R. Brady, Angle Orthod. 42 (1972) 172.
[3] G.F. Andreasen, R.E. Morrow, Am. J. Orthod. 73 (1978) 142.

[4] C.J. Burstone, B. Qin, J.Y. Morton, Am. J. Orthod. 87 (1985) 445.
[5] F. Miura, M. Mogi, Y. Ohura, H. Hamanaka, Am. J. Orthod. Dentofacial Orthop. 90 (1986) 1.
[6] S.E. Khier, W.A. Brantley, R.A. Fournelle, Am. J. Orthod. Dentofacial Orthop. 99 (1991) 310.
[7] C.M. Wayman, T.W. Duerig, in: T.W. Duerig, K.N. Melton, D. Stöckel, C.M. Wayman (Eds.), Engineering Aspects of Shape Memory Alloys, Butterworth–Heinemann, London, 1990, p. 3.
[8] T.W. Duerig, R. Zadno, in: T.W. Duerig, K.N. Melton, D. Stöckel, C.M. Wayman (Eds.), Engineering Aspects of Shape Memory Alloys, Butterworth–Heinemann, London, 1990, p. 369.
[9] R.C.L. Sachdeva, S. Miyazaki, in: T.W. Duerig, K.N. Melton, D. Stöckel, C.M. Wayman (Eds.), Engineering Aspects of Shape Memory Alloys, Butterworth–Heinemann, London, 1990, p. 452.
[10] W.A. Brantley, in: W.J. O'Brien (Ed.), Dental Materials and Their Selection, 2nd Edition, Quintessence, Chicago, 1997, p. 273.
[11] K. Otsuka, in: T.W. Duerig, K.N. Melton, D. Stöckel, C.M. Wayman (Eds.), Engineering Aspects of Shape Memory Alloys, Butterworth–Heinemann, London, 1990, p. 36.
[12] T. Yoneyama, H. Doi, H. Hamanaka, Y. Okamoto, M. Mogi, F. Miura, Dent Mater. J. 11 (1992) 1.
[13] T.G. Bradley, W.A. Brantley, B.M. Culbertson, Am. J. Orthod. Dentofacial Orthop. 109 (1996) 589.
[14] T. Todoroki, H. Tamura, Trans. Jpn. Inst. Metals 28 (1987) 83.
[15] T.A. Thayer, M.D. Bagby, R.N. Moore, R.J. De Angelis, Am. J. Orthod. Dentofacial Orthop. 107 (1995) 604.
[16] R. Chen, Y.F. Zhi, M.G. Arvystas, Angle Orthod. 62 (1992) 59.
[17] W.A. Brantley, M. Iijima, unpublished research.