Differential Scanning Calorimetry (DSC) Analyses Of Superelastic And Nonsuperelastic Nickel-Titanium Orthodontic Wires

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Abstract: The purpose of this study was to determine the transformation temperatures for the austenitic, martensitic, and rhombohedral (R) structure phases in representative as-received commercial nitinol (NiTi) orthodontic wire alloys, to reconcile discrepancies among recent publications. Specimens were examined by differential scanning calorimetry (DSC) over a temperature range from approximately −170° C to 100° C, with a scanning rate of 10° C

per minute. Two different pathways, with the intermediate R structure either absent or present, were observed for the transformation from martensitic to austenitic NiTi, whereas the reverse transformation from austenitic to martensitic NiTi always included the R structure. The enthalpy (ΔH) for the transformation from martensite to austenite ranged from 0.3 to 35 calories per gram. The lowest ΔH value for the nonsuperelastic Nitinol wire is consistent with a largely work-hardened, stable, martensitic microstructure in this product. The DSC results indicate that the transformation processes are broadly similar in superelastic, body-temperature shape-memory, and nonsuperelastic NiTi wires. Differences in bending properties for the NiTi orthodontic wires at room temperature and 37° C are due to the relative proportions of the metallurgical phases in the microstructures.

Commercial nickel-titanium orthodontic wires fabricated from near-equiatomic NiTi (nitinol) compositions were introduced during the 1970s, after the pioneering research of Andreasen and coworkers.[1,2] The mechanical properties and clinical characteristics of the original NiTi product, marketed as Nitinol by the Unitek Corporation, were reported by Andreasen and Morrow.[3] This wire has a very low elastic modulus, as well as an extremely wide working range and excellent spring-back (using a 12.5 mm cantilever bending test span), thus providing much lighter and more constant forces over an extended treatment period, compared with the use of conventional stainless steel wires. In additional publications, Andreasen and his colleagues described the force delivery and temperature dependence for nitinol wires.[4-6]

Subsequently, Burstone et al.[7] and Miura et al.[8] introduced the Chinese and Japanese NiTi wires, respectively, to the specialty. These wires, now marketed as Ni-Ti (Ormco/Sybron, Glendora, Calif.) and Sentinol or Sentalloy (GAC International, Central Islip, N.Y.), displayed superelastic characteristics, where the deactivation plot contains an extended region of largely constant bending moment or tensile stress.[7,8] By using a cantilever bending test span (6 mm) similar to interbracket distances, Khier et al.[9] found that commercial NiTi orthodontic wires could be classified as superelastic or nonsuperelastic, where the latter products had much lower springback. The superelastic wires were reported to be austenitic NiTi and underwent a reversible stress-induced transformation to martensitic NiTi during activation, whereas the nonsuperelastic wires, such as Nitinol, had stable work-hardened martensitic structures.[8] Later, Leu et al.[10] employed differential scanning calorimetry (DSC) to show that the phase

transformations in the superelastic NiTi wires were more complex and involved an immediate rhombohedral (R) structure.[11,12]

However, recent research has suggested that these concepts for the metallurgical structures and phase transformations in orthodontic NiTi alloys may require some revision. By using x-ray diffraction (XRD) to analyze wires in the as-received condition and after tensile strain, Thayer et al.[13] identified XRD peaks for the martensitic NiTi structure and concluded that the nonsuperelastic wires principally have the austenitic structure at room temperature. This conclusion was supported by the very low martensitic transformation temperatures obtained by Chen et al.[14] from electrical resistivity measurements, where the M_s and M_f temperatures for the start and finish of this transformation were typically below $-40°$ and $-100°$ C, respectively. These transformation temperatures were much lower than those obtained from DSC measurements for orthodontic alloys[10,15,16] and found in the materials science literature.[17,18]

The purpose of this study was to reconcile these conflicting results by carefully examining the DSC heating and cooling curves for several representative commercial NiTi wires. The aim was to characterize the phase transformation processes in these different products, specifically seeking evidence of very low temperature martensite transformations. Specimens evaluated with the present DSC apparatus could be cooled to approximately $-170°$ C, which was not possible in the previous extensive study by Leu et al.[10]

Materials and methods

The commercial NiTi alloys selected for study are summarized in Table

Table I. The nickel-titanium orthodontic wires used in the study

Wire product	Size (inch)	Manufacturer
Nitinol SE	0.016	Unitek/3M, Monrovia, Calif.
Ni-Ti	0.016	Ormco/Sybron, Glendora, Calif.
Neo Sentalloy	0.016 × 0.022	GAC International, Central Islip, N.Y.
Titanal LT	0.018	Lancer Orthodontics, Carlsbad, Calif.
Nitinol	0.016	Unitek/3M, Monrovia, Calif.

I.

All wires were contributed by the manufacturers in standard arch blank forms. Two of these products are superelastic (Nitinol SE,

Unitek, Monrovia, Calif., and Ni-Ti),[7-9] and the Nitinol wire (Unitek, Monrovia, Calif.) is nonsuperelastic.[3,9] Fletcher et al.[16] have shown that the Neo Sentalloy wire has shape-memory (superelastic) behavior at 37° C, but not at room temperature (22° C). The Titanal LT product (Lancer Orthodontics, Carlsbad, Calif.) is advertised as a body-temperature, heat-activated nickel-titanium wire with shape-memory capability, and was thus expected to have characteristics very similar to those for Neo Sentalloy. The clinically popular 0.016-inch diameter size selected for Nitinol SE, Ni-Ti, and Nitinol has been used in other studies[7-9] of these wires. For the Titanal LT alloy, 0.018-inch diameter wires were used due to the unavailability of the 0.016-inch diameter size. For Neo Sentalloy (available only in rectangular cross-sections), the popular 0.016 × 0.022-inch size was selected.

The wire specimens were carefully cut with a water-cooled, diamond-embedded saw (Vari/Cut VC-50, Leco Corp., St. Joseph, Mich.). Considerable care was taken in cutting the samples so that minimal heat and stress would be generated. Straight segments of 5 mm length were cut from each arch blank, and five segments of each wire were weighed (~20 mg sample size) with an electronic balance and placed in an aluminum pan. The 5 mm segment length was selected because of the pan dimensions, and pilot experiments indicated that the use of five segments yielded excellent thermal contact within the sample and DSC spectra of high resolution. Shorter wire segments were not used to minimize the amount of cutting required for sample preparation. There is no consensus in previous studies about the ideal DSC sample weight for the NiTi wire segments, and the present size was intermediate between those used by Todoroki and Tamura (10 mg)[17] and by Yoneyama et al. (40 mg).[15]

For the differential scanning calorimetry experiments (TA 910, TA Instruments, Wilmington, Del.), each sample of five wire segments was initially cooled from room temperature to −170° C and then heated to 100° C at a scanning rate of 10° C/min. Subsequently, the sample was cooled again to approximately −170° C at the same scanning rate, and the same heating and cooling cycles were repeated a second time. Pilot experiments established that excellent reproducibility was achieved between nominally identical five-segment samples of the same NiTi alloy, so that the procedure of a single sample and replicate DSC heating and cooling runs was adopted for

the present experiments. Dry nitrogen gas was used to flush the specimen chamber, to prevent condensation of water vapor and oxidation of the NiTi wires. A second, empty aluminum pan served as an inert reference, and the apparatus was calibrated with an indium standard, as well as by the melting point of water.

In the DSC procedure, the differential heat flow required to heat or cool the experimental and reference samples at the same scanning rate is recorded as a function of temperature to yield the spectrum or thermogram. The start and finish temperatures of each phase transformation were determined from tangent lines where the DSC curve deviates from the adjacent baselines. Individual or combined peak areas (enthalpies) were calculated from a peak on the DSC plot whose area had previously been analyzed by the computer software. Segments of beta-titanium arch wire and a polycrystalline alumina bracket, which do not undergo phase transformations over this temperature range, served as inert controls to establish the resolution of the apparatus.

Results

Representative DSC curves for the NiTi wires studied are shown in Figs. 1 to
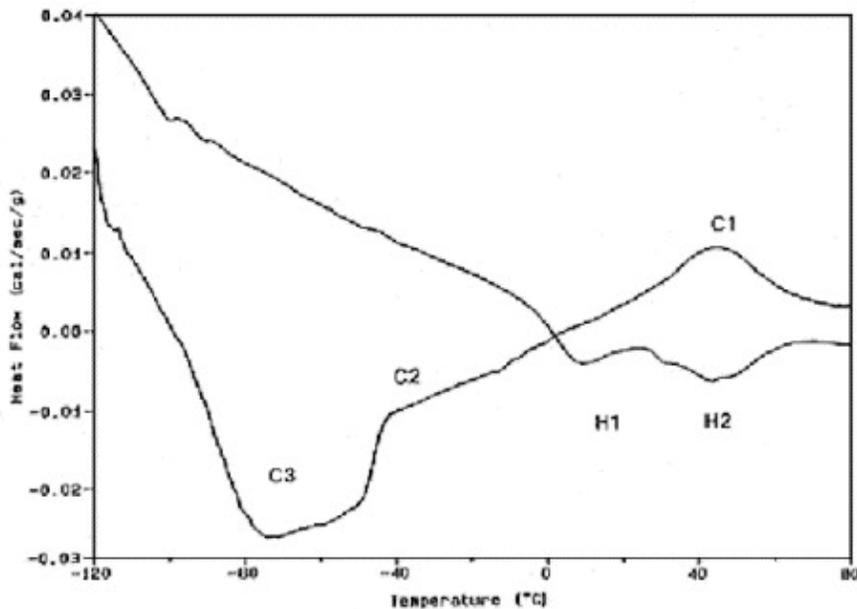
5.

Fig. 1. DSC heating and cooling curves for Nitinol SE (Unitek). *H1* and *H2* peaks are indicated for heating curve, and *C1* and *C2* peaks are shown for cooling curve, along with possible position of very poorly resolved *C3* peak.

Apparent substructure in *H2* peak is attributed to instrumentation noise. Area under peak (enthalpy change ΔH for phase transformation) is determined with respect to extrapolated baselines from adjacent portions of curve.
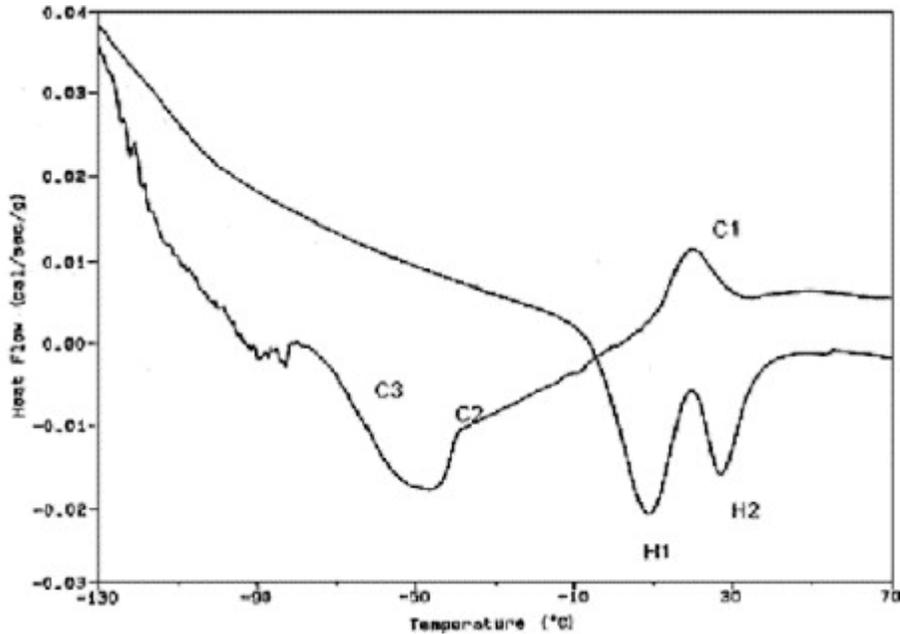

Fig. 2. DSC heating and cooling curves for Ni-Ti (Ormco). Curves are similar in general appearance to those in Fig. 1**Fig. 1**Fig. 1, although phase transformations occur over different temperature ranges. Fluctuations in cooling curve below *C3* peak are due to instrumentation noise.
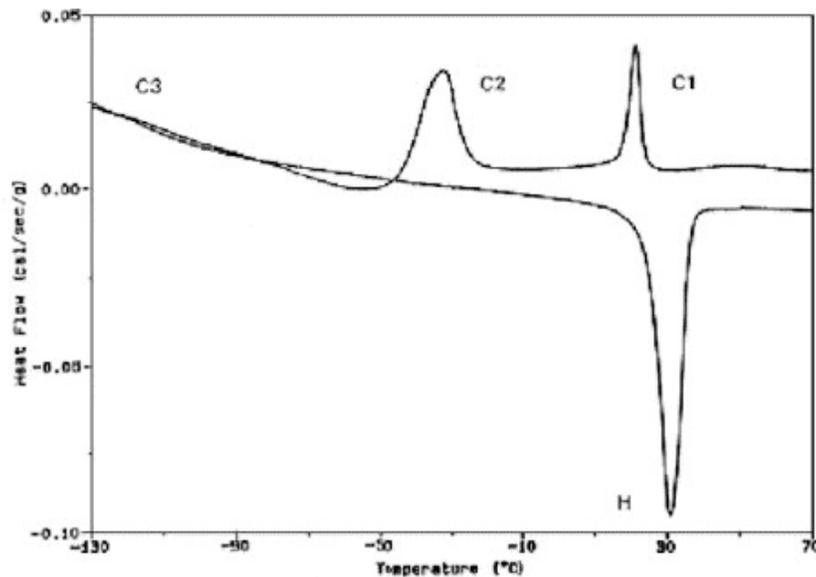

Fig. 3. DSC heating and cooling curves for Neo Sentalloy (GAC). Note that only one endothermic peak (H) is found on heating curve, in contrast to Figs. 1 and 2**Figs. 1 and 2**Figs. 1 and 2.

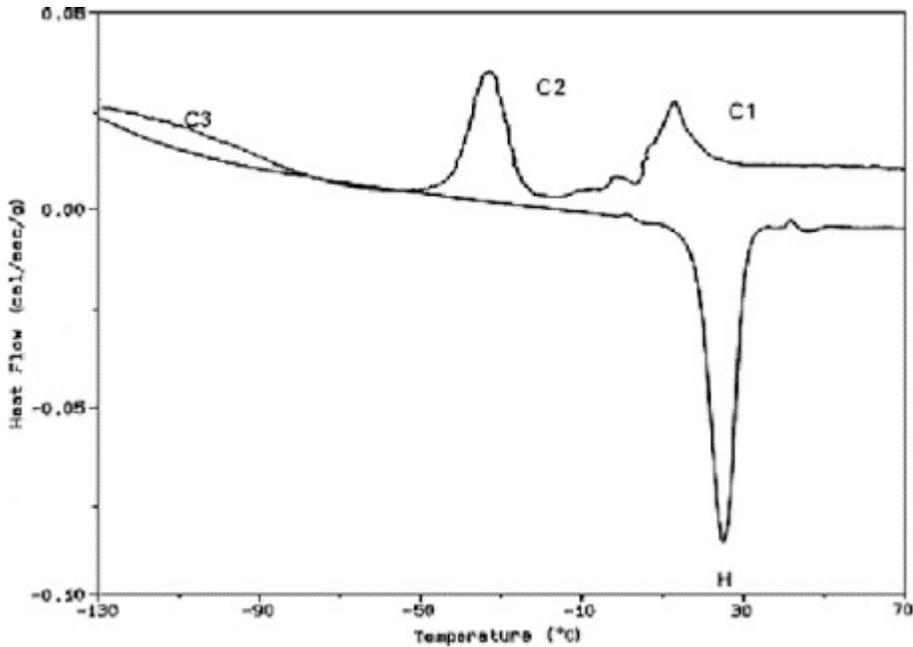Fig. 4. DSC heating and cooling curves for Titanal LT (Lancer). Small fluctuations in curves are attributed to instrumentation noise. Phase transformation characteristics are similar for those for Neo Sentalloy in Fig. 3**Fig. 3**Fig. 3.
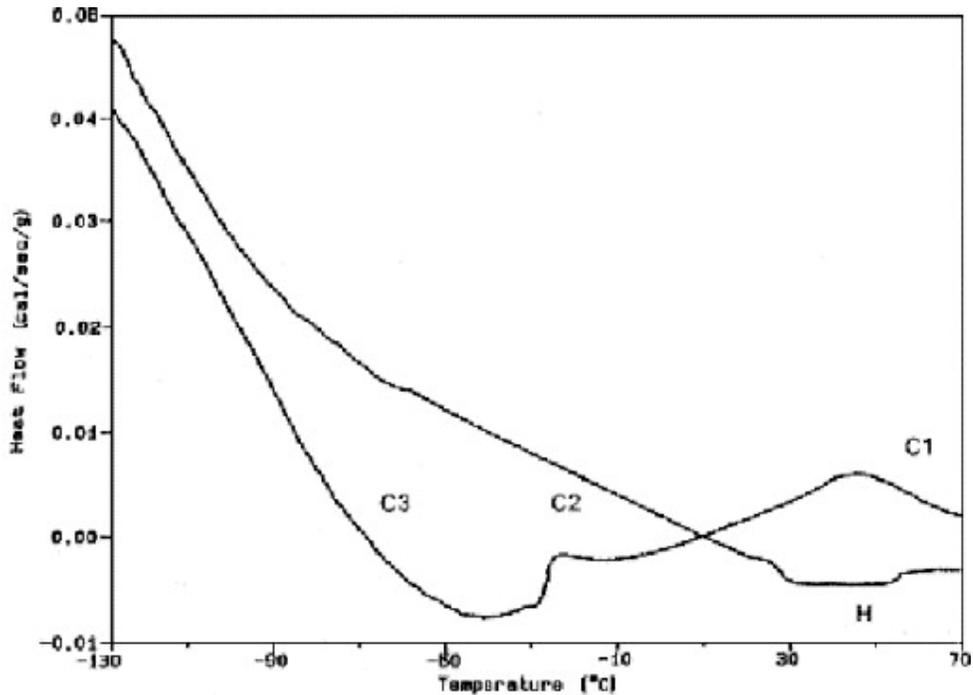

Fig. 5. DSC heating and cooling curves for Nitinol (Unitek). Area under *H* peak is much smaller than areas under peaks on heating curves for other NiTi alloys (**Table II**).

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Table II. Transformation temperatures and enthalpy changes (ΔH) for NiTi orthodontic wires

Wire brand	Cooling (°C)*					Heating (°C)**		ΔH (calories per gram)
	M_{s1}	M_{f1}	M_{s2}	R_s	R_f	A_s	A_f	
Nitinol SE	−19	−46	−70	59	21	−4	63	1.5
Ni-Ti	−25	−43	−60	30	10	−13	40	3.0
Neo Sentalloy	−22	−49	−70	22	13	19	36	3.5
Titanal LT	−22	−48	−80	24	2	12	34	3.5
Nitinol	−12	−28	−50	55	25	22	55	0.3

*For the cooling DSC curves, the R_s and R_f temperatures correspond to the A-R transformation (C1 peak). The M_{s1} and M_{f1} temperatures correspond to the R-M transformation (C2 peak). The highly approximate starting temperature for the poorly resolved, martensitic C3 peak is designated as M_{s2}, and there was no evidence for the M_{f2} temperature.

**For the heating DSC curves, the A_s and A_f temperatures and ΔH value include both the M-R and R-A transformations in Figs. 1 and 2, and the single M-A transformation in Figs. 3 to 5. Figs. 1 and 2 should be consulted for the temperatures corresponding to the individual M-R and R-A transformations.

Two peaks (Figs. 1 and 2) or one peak (Figs. 3 to 5) were observed on the heating curves, and these endothermic peaks have been labeled as H1 and H2, or as H, respectively. From the analysis of Todoroki and Tamura,[17] the H1 and H2 peaks are interpreted as the transformations from martensite to R structure (M-R) and from R structure to austenite (R-A), while the H peak corresponds to the direct transformation from martensite to austenite (M-A). Two exothermic peaks (C1 and C2) observed on all cooling curves are interpreted[17] as the reverse transformations of austenite to R structure (A-R) and R structure to martensite (R-M), respectively.

An additional low temperature peak (C3) appeared to occur near the limit of resolution for Ni-Ti (Fig. 2) and Titanal LT (Fig. 4). Locations of possible C3 for Nitinol SE (Fig. 1), Neo Sentalloy (Fig. 3), and Nitinol (Fig. 5) have been placed near the cooling curves, but these peaks cannot be resolved by DSC. If it exists, the C3 peak is assumed to represent an additional phase transformation within the complex martensitic structure.[17]

Table II summarizes the temperature ranges for all cooling transformations, along with the temperatures and enthalpy changes for the overall heating transformation from martensite to austenite. Under the present experimental conditions, the temperatures in Table II are considered to have an accuracy of approximately ± 2° C and the enthalpy values have been rounded to the nearest 0.5 calories per gram except for Nitinol. For Nitinol SE and Ni-Ti, the A_s, A_f and ΔH values correspond to both the H1 and H2 peaks in Figs. 1 and 2.

Highly approximate M_{s2} temperatures have been estimated for the C3 peaks, and no M_{f2} temperature could be resolved for any alloy.

Referring to Figs. 1 and 2, the two peaks in both the heating and cooling curves for Nitinol SE and Ni-Ti indicate that the R structure forms as an intermediate phase during the reversible M-A transformation. The phase transformation temperatures differed somewhat for these two alloys, as shown in Table II. Thermal analyses of the two controls (beta-titanium and alumina) indicated that the substructure in the H2 peak for Nitinol SE and the fluctuations on the cooling curve below the C3 peak for Ni-Ti were due to instrumentation noise.

The curves for Neo Sentalloy in Fig. 3 show transformation temperature ranges similar to those reported by Fletcher et al.,[16] except that an unresolved pair of peaks for the M-R and R-A transformations were observed in the earlier study. Although exhibiting some instrumentation noise, the curves for Titanal LT in Fig. 4 resemble those for Neo Sentalloy, and the transformation temperatures were similar. During cooling, the R structure has a role in the A-M transformation for these shape-memory alloys, but apparently not for the heating cycle where only a single H peak was observed. Lastly, for the nonsuperelastic wire Nitinol a single broad, weak peak occurred during the heating cycle, and two weak peaks were observed during the cooling cycle.

Discussion

When the present DSC phase transformation temperatures in Table II are compared with those determined by Chen et al.[14] from the temperature dependence of electrical resistivity, there is general agreement for the two NiTi wires (Ormco Ni-Ti and Nitinol) common to both studies. The present A_s, A_f and R_s temperatures for Nitinol are close to the temperatures reported by Chen et al. (who did not provide R_f temperatures). For the Ni-Ti alloy, Chen et al. reported differences in the phase transformation temperatures for the original Chinese NiTi[7] and the Ormco Ni-Ti product,[9] which may be attributed to differences in the two manufacturing processes. Fariabi et al.[18] have shown that variations in the amount of cold work and the heat treatment temperature can have substantial effects on the phase transformation

temperatures for a near-equiatomic NiTi alloy. The present data in Table II generally show better agreement with the Chen et al. transformation temperatures for Chinese NiTi. Comparison of the present results for Titanal LT is not possible, since Chen et al. used the original Titanal[9] product in their study.

Excellent agreement was found for the as-received Ni-Ti alloy between the present C1 peak in Fig. 2 and the single peak observed by Leu et al.[10] during cooling. This latter study used an apparatus (DSC-3 Perkin-Elmer, Norwalk, Conn.) where specimens were cooled by dry ice, and the minimum useful temperature on the DSC plots was approximately 0° C. There was also excellent agreement between the H2 peak in Fig. 2 and the single peak on their heating DSC curve. Any lower temperature peak on their heating curve would have been inaccessible and at substantial variance with the H1 peak in Fig. 2. The present C2 peak was also inaccessible with their apparatus.

Although the usual phase transformations in cold-worked near-equiatomic nonorthodontic NiTi alloys involve one or two peaks on the heating and cooling DSC curves,[17,18] Todoroki and Tamura[17] also observed three peaks on the cooling curves under certain heat treatment and thermal cycling conditions. They noted that other investigators had proposed the occurrence of a complex series of martensitic reactions in NiTi alloys. Todoroki and Tamura also found that electrical resistivity measurements provided much lower resolution than DSC for the study of phase transformations in NiTi alloys and that the two techniques did not yield the same transformation temperature ranges and peaks. An additional advantage of DSC is that the enthalpy change for a phase transformation can be determined, which is not possible with electrical resistivity measurements.

The present observation that the nonsuperelastic Nitinol wire is largely martensitic at room temperature (Fig. 5) is in agreement with other investigators,[8,9,15] including x-ray diffraction studies by Khier et al.[19] However, this conclusion is contradictory to Thayer et al.,[13] whose XRD experiments with wires subjected to tensile strain suggested that as-received Nitinol has the austenitic structure at room temperature. Certain martensite variants (orientations)[20] should be favored when NiTi orthodontic wires undergo substantial tensile strain. Thus the

martensite peaks observed by Thayer et al. after tensile loading may be different from those in the as-received wires studied by Khier et al., where the work-hardened martensitic structure and preferred crystallographic orientation resulting from the manufacturing processes would yield different combinations of variants. Research is needed to establish the metallurgical structures of orthodontic NiTi wires and coil springs[21] for the as-received condition and after heat treatment (conveniently performed by the direct electrical resistance technique[16,22]), and with clinical use where practical levels of deformation are encountered.

Although phase transformation processes in NiTi orthodontic wires are more conveniently studied by DSC than XRD, the DSC results in this study have demonstrated the complexity of the transformation processes between austenite and martensite in the various types of commercial NiTi orthodontic wires. Otsuka[12] has discussed the R structure, which appears to be an intermediate phase for both the M-A and A-M transformation directions in Nitinol SE and Ni-Ti but seems to only participate in the A-M transformation path in Neo Sentalloy, Titanal LT, and Nitinol. The broad H peak for Nitinol may correspond to two successive transformations involving the R structure, but there was insufficient DSC resolution of this very low energy peak.

Although there is an energy difference between the overall M-A and A-M transformations in NiTi alloys,[20] the total enthalpy changes associated with the peaks on the heating and cooling curves in Figs. 1 to 5 appear to be similar. However, such comparisons are approximate because of the difficulty in accurately defining the DSC peak positions, particularly any C3 peak. Lee et al.[23] found that the enthalpy change for the exothermic A-M transformation was about 60% of that for the endothermic M-A transformation in NiTi alloys; these investigators observed only a single peak in the cooling and heating DSC curves.

Hysteresis, the temperature difference between the forward and reverse transformations in NiTi alloys,[20] is evident when corresponding peaks on the heating and cooling curves are compared. The C1 peak (A-R) occurs at lower temperatures than the H2 peak (R-A) in Ni-Ti in Fig. 2, or than the H peaks (M-A) for Neo Sentalloy and Titanal LT in Figs. 3 and 4. However, there is little difference in the temperatures of

the C1 and H2 peaks for Nitinol SE in Fig. 1, and the C1 and H peaks for Nitinol in Fig. 5. For all five alloys, there is a considerable difference between the temperature ranges for the C2 peak (R-M) and either the H1 (M-R) or H peaks. Moreover, there is no counterpart on the heating DSC curves for the C3 peak.

Examination of several DSC plots published by Todoroki and Tamura[17] and by Fariabi et al.[18] reveals that the areas under the R structure peaks for the forward (R-A) and reverse (A-R) transformations involving austenite can be either greater or less than the areas under the forward (M-R) and reverse transformations (R-M) involving martensite. The present ΔH values of 0.3 to 3.5 calories per gram in Table II for the endothermic transformation from martensite to austenite (H peak or the sum of the H1 and H2 peaks) are in good agreement with recent values reported by Yoneyama et al.[15] from DSC studies of seventeen commercial NiTi alloys. These latter authors measured values of ΔH (typically for the combined M-R and R-A transformations) ranging from 1.0 to 4.9 calories per gram, but reported no endothermic M-A transformation for Nitinol similar to the very weak peak in Fig. 5. Fariabi et al.[18] found that the endothermic ΔH values ranged from 3.6 to 5.7 calories per gram for cold-worked and heat-treated nonorthodontic alloys.

Comparison of phase transformations for orthodontic NiTi wires with NiTi alloys in the materials science literature is hindered by their dependence on the amount of cold work, heat treatment temperature, and Ni/Ti ratio. Todoroki and Tamura[17] and Fariabi et al.[18] have presented extensive data on the complex influences of cold work and heat treatment on the transformation pathways and enthalpy changes. These two critical factors are expected to vary among the different manufacturers for orthodontic NiTi products and would account for the differences observed by Chen et al.[14] for Chinese NiTi and the equivalent Ormco Ni-Ti. Melton and Mercier[24] have shown that varying the alloy composition from 54.5% to 55.5 wt% nickel causes the M_s temperature to decrease from 57° C to −30° C, with a decrease in the hysteresis between the forward and reverse transformations from 55° to 32°. Thus small variations in the manufacturing procedures for the NiTi wires can have enormous effects on the phase transformations. The incompletely resolved H1 and H2 peaks previously observed by Fletcher et al.[16] for Neo Sentalloy could be due to manufacturing

differences for the two batches of arch wires, although differences in specimen preparation cannot be excluded. Considerable care was taken to minimize stress and heating during preparation of the present DSC samples since previous research has shown that both stress and heat treatment at temperatures of 500° C and 600° C profoundly affect the bending properties and metallurgical structures of the superelastic wires.[8-10] However, little effect was observed after the heat treatment of nonsuperelastic wires.[9]

The heating DSC curves in Figs. 1 to 5 can be used to predict the metallurgical phases in the as-received NiTi wires at room temperature and 37° C. For the two room temperature superelastic wires, Nitinol SE and Ni-Ti, the conversion to austenite (H1 peak) started at much lower temperatures than for the other three products (H peak). For the two body-temperature shape-memory (superelastic) wires, Neo Sentalloy and Titanal LT, the A_f temperatures (H peak) were below 37° C, although the A_s temperatures were much higher than those for Nitinol SE and Ni-Ti. The heating DSC curves suggest that Ni-Ti, Neo Sentalloy and Titanal LT should be almost or completely austenitic in the oral environment, whereas Nitinol SE should be a mixture of austenite and R structure. The nonsuperelastic Nitinol should be entirely or almost entirely martensitic at room temperature, although this product would be partially transformed to austenite at mouth temperature. Alternatively, if the cooling DSC curves are used to predict the phases, Ni-Ti, Neo Sentalloy and Titanal LT would be austenitic at 37° C, whereas Nitinol SE and Nitinol would be mainly R structure with some austenite present; at room temperature, both Nitinol SE and Nitinol would be almost entirely R structure. These predictions of phases from the DSC curves require verification by some other technique, since the procedure of initially cooling the samples to very low temperatures before commencing the dynamic heating and cooling cycles may yield different proportions of the metallurgical phases in these wires than those appropriate to clinical conditions.

The foregoing DSC analyses of the metallurgical structures in these representative alloys appear to suggest that the body-temperature shape-memory NiTi wires are advantageous clinically in comparison to the other superelastic and nonsuperelastic wires. Although the nonsuperelastic wires have excellent springback and

elastic ranges compared with orthodontic alloys other than nickel-titanium,[3,9,25] these NiTi wires have a work-hardened martensitic structure and cannot take advantage of the transformation from martensite to austenite that is required for superelastic and shape-memory behavior. Andreasen and Hilleman[1] originally stressed the importance of the shape-memory property for clinical orthodontics, noting that the temperature range for transition to austenite should lie between room temperature and mouth temperature. Consequently, it would appear that NiTi wires that are heat-sensitive in the oral environment would provide a more clinically desirable combination of light, continuous, and physiologic force levels. Use of refrigeration would convert the shape-memory wires to the more deformable martensitic structure, which may facilitate initial engagement into severely malpositioned teeth under clinical conditions. Subsequent thermal activation in the oral environment would transform these wires to the fully austenitic structure, where light and continuous forces are delivered with optimal springback characteristics compared with the other types of commercially available products. Recently, a new type of shape-memory wire has been introduced, where copper has been incorporated in the NiTi alloy composition to alter the transition temperature range (TTR) to austenite, lower or raising the TTR between room and mouth temperature to modify the clinical activity of the wire. If the TTR is above the temperature of the oral environment, this wire would be active only when hot foods or liquids are ingested and would thus be suitable for a treatment case where limited activity is desired. Clinical trials comparing different types of NiTi wires are required to verify these hypotheses.

Conclusions

Under the experimental conditions of this study, the following conclusions can be drawn:

1. The five representative commercial NiTi orthodontic wires examined undergo similar phase transformations over the temperature range of −170° C to 100° C. A martensitic transformation peak with a starting temperature from about −50° C to −80° C may exist in these alloys, but was near the limit of resolution for the DSC technique employed.

2. The superelastic NiTi alloys (Nitinol SE and Ni-Ti) undergo austenitic transformations involving the R structure which begin below 0° C. The DSC analyses indicate that in the oral environment Ni-Ti is almost entirely austenite, whereas Nitinol SE is a mixture of austenite and R structure.

3. The nonsuperelastic alloy Nitinol is entirely or almost entirely martensite at room temperature, and contains small additional amounts of austenite in the oral environment.

4. The phase transformation characteristics for Neo Sentalloy and Titanal LT are similar and consistent with their reported shape-memory characteristics. These wires are entirely or almost entirely austenite at body temperature.

5. The enthalpy changes measured by DSC for the transformations from martensite to austenite were in good agreement with the previously reported range for NiTi orthodontic wires. The proportions of the metallurgical phases should be verified by XRD or electron diffraction, or by the measurement of electrical resistivity changes.

Acknowledgements

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