Original Article

Thermal Analysis of As-received and Clinically Retrieved Copper-nickel-titanium Orthodontic Archwires

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ABSTRACT

Objective: To compare as-received copper-nickel-titanium (CuNiTi) archwires to those used in patients by means of differential scanning calorimetry (DSC). Also, the thermal or phase properties of 27°C, 35°C, and 40°C CuNiTi archwires were studied to ascertain if their properties match those indicated by the manufacturer.

Materials and Methods: Six wires of 27°C, 35°C, and 40°C CuNiTi were tested as-received, and six each of the 27°C and 35°C wires were examined after use in patients for an average of approximately 9 and 7 weeks, respectively. Segments of archwire were investigated by DSC over the temperature range from −100°C to 150°C at 10°C per minute.

Results: There were no significant differences between as-received and clinically used 27°C and 35°C wires for all parameters (heating onset, endset, and enthalpy and cooling onset, endset, and enthalpy), except the 27°C wires exhibited a significant decrease in the heating enthalpy associated with the martensite-to-austenite transition after clinical use. The heating endsets (austenite finish temperatures) of the 27°C and 35°C wires were within 2°C of those claimed by the manufacturer, but the 40°C wires were found to be nearer to 36°C than 40°C.

Conclusions: Clinical use of CuNiTi wires resulted in few differences when compared with as-received wires analyzed by DSC. Two temperature varieties of CuNiTi are reasonably within the parameters of those identified by the manufacturer.

KEY WORDS: Thermal analysis; DSC; Copper-nickel-titanium; Archwires

INTRODUCTION

Copper-nickel-titanium (CuNiTi) archwires are a relatively new tool in the armamentarium of orthodontists. They were introduced in 1994 by Ormco and can be manufactured to transform between the pliable (martensitic) and the shape-retaining (austenitic) crystalline structures at different temperatures (27°C, 35°C, and 40°C). Thus, they are body heat–activated archwires that are more easily engaged at room temperature and become functional at the temperatures encountered in the mouth.[1–9]

CuNiTi wires are marketed to orthodontists regarding their different properties, including intermittent force delivery, with various transformation temperatures. With the increasing popularity of these wires, these claims need to be investigated. Some mechanical studies have been conducted and have shown that CuNiTi wires exhibit less change in their stress-strain curves because of cyclic deformation than the most stable binary NiTi alloy.[10] They also have a narrower stress hysteresis and more stable transformation temperature and delivery of force.[11] Hence, these wires also aid in the movement of teeth through light continuous force, which avoids hyalinization of the periodontal membrane, necrosis, undermining resorption, and loss of anchorage and decreases the likelihood of root resorption.[12,13]

Differential scanning calorimetry (DSC) is a thermal analysis technique where a sample may be cycled through a range of temperatures at a highly controlled rate. Information is elucidated when comparing the amount of heat necessary to maintain the rate of tem-

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perature change of the sample relative to an inert reference. Phase changes in materials are accompanied by the production or absorption of energy. These events present as peaks on the heat flow temperature graphs (DSC thermograms), which can be analyzed for the beginning temperature, area below the peak, and end temperature. On heating superelastic NiTi wires, these events have represented the austenitic start temperature (A_s), change in enthalpy (ΔH) of the phase transformation, and austenitic finish temperature (A_f) of the endothermic peak. The cooling equivalents are the martensitic start temperature (M_s), ΔH on cooling, and martensitic finish temperature (M_f) of the exothermic peak. Which one of the three phases of NiTi alloys (martensite, the intermediate rhombohedral or R-phase, and austenite) that exist at a given temperature are revealed as well.

Several DSC studies have been performed on NiTi archwires[14,15] as well as on a single-temperature variant of CuNiTi.[5,16,17] In addition, DSC has also been used to study NiTi endodontic files,[18] with one study investigating whether a simulated clinical use altered the thermal or phase transition properties of the NiTi file.[19] Although no differences were noted when comparing the new files and those that underwent simulated clinical use, there are considerable differences in the forces, environment, and duration of use experienced by endodontic files and orthodontic archwires.[20–22] Mallory et al[23] and anecdotal reports have observed a "dead wire" phenomenon with some 35°C CuNiTi wires after retrieval from the mouth, implying that an alteration of the thermal or phase transition properties of the wire occurred. Given this and that differences that could prove clinically relevant have been observed in NiTi wires after simulated and actual clinical use,[5,16,17,24,25] a calorimetric study investigating the thermal or phase transition properties of orthodontic wires after clinical use in the oral environment appears warranted.

The purpose of this study was to investigate by DSC any differences between as-received and clinically retrieved CuNiTi wires after several weeks of use in patients. The differing thermal or phase transition properties of the three variations of CuNiTi (27°C, 35°C, and 40°C) orthodontic archwires, which have yet to be presented together in the peer-reviewed literature,[26] will also be presented.

MATERIALS AND METHODS

The three temperature variants (27°C, 35°C, and 40°C) of CuNiTi orthodontic archwires (Ormco, Glendora, Calif) were studied in the clinically popular dimension of 0.016 × 0.022 inches. Six wires of each type were analyzed by DSC in their as-received condition. In addition, for each of the 27°C and 35°C variants, six wires were analyzed after being used in patients during normal orthodontic treatment. The time period in the mouth varied from 1 to 3 months. These wires were from matched lot numbers with those tested in the as-received condition.

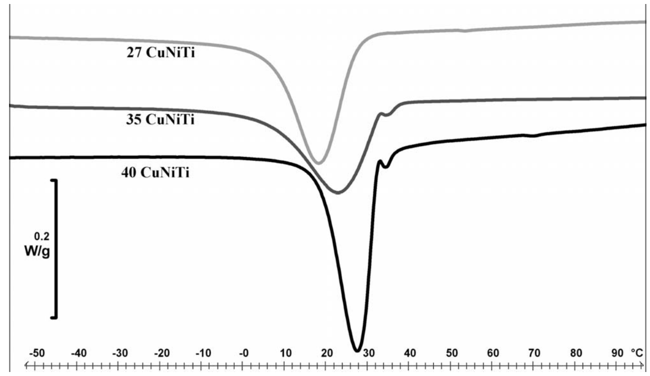

Figure 1. Differential scanning calorimetry heating curves for as-received 27°C, 35°C, and 40°C copper-nickel-titanium archwires.

Specimen preparation for DSC analysis consisted of sectioning a 5-mm segment from the premolar area of each archform. This area was chosen because it is a relatively straight segment and thereby most likely experiencing fewer stresses during manufacturing, activation, and clinical use. The wires were sectioned with a low-speed water-cooled diamond saw (Isomet, Buehler Ltd, Lake Bluff, Ill) with care taken to avoid mechanical stresses and heating that would alter the microstructure of the wire.

The wire segment was weighed to the nearest 0.01 mg, placed in an aluminum crucible, and sealed. An empty aluminum crucible served as the reference during DSC measurement (Model 822[e], Mettler–Toledo Inc, Columbus, Ohio). The temperature of the crucibles was scanned from −100°C to 150°C, with liquid nitrogen as coolant and nitrogen gas for purging, at 10°C per minute for the heating curve and then cooled at the same rate from 150°C to −100°C for the cooling curve. The DSC plots were qualitatively and quantitatively analyzed by the DSC manufacturer's software. ΔH, along with onset and endset temperatures, for the various phase transformations were calculated. Statistical analysis consisted of one-way analysis of variance (ANOVA) (SPSS Inc, Chicago, Ill) and post hoc Tukey test for the as-received wires. For the as-received and clinically used matched wire pairs, a paired Student's *t*-test was performed. Statistical significance was set at $P = .05$.

RESULTS

Figures 1 and 2 display thermograms of as-received 27°C, 35°C, and 40°C CuNiTi for heating and

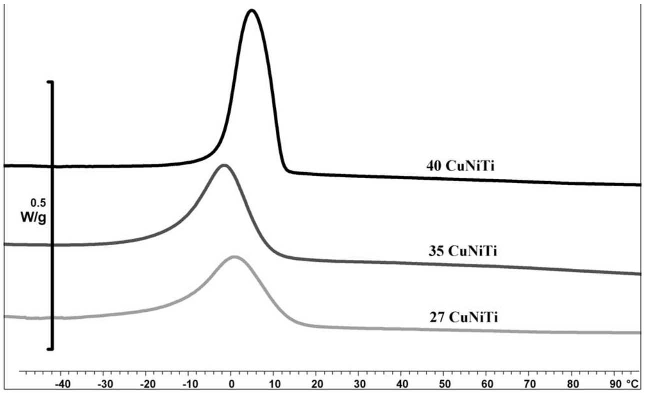

Figure 2. Differential scanning calorimetry cooling curves for as-received 27°C, 35°C, and 40°C copper-nickel-titanium archwires.

cooling, respectively. For the heating curves, qualitative differences were observed among the three CuNiTi temperature variants. On heating, all 40°C CuNiTi wires had two overlapping peaks corresponding to the martensite-to-R-phase transition (larger, lower temperature peak) and the R-phase-to-austenite transition (smaller peak on the shoulder of the previous). Five of six 35°C and two of six 27°C as-received CuNiTi wires showed the intermediate R-phase peak also but of smaller intensities, respectively. In Figure 1, the curve for the 27°C wire is representative of the four specimens not showing the R-phase transition. The cooling curves for all three varieties of CuNiTi were qualitatively similar in that only one peak was observed.

Table 1 lists the mean and standard deviation heating onset temperature; endset temperature; and enthalpy for transformations in the 27°C, 35°C, and 40°C CuNiTi wires tested, whereas Table 2 lists the corresponding values for cooling. Also listed in the tables is the duration of clinical usage for the clinically retrieved wires. The six 35°C wires were in use for an average of 47 days, whereas the six 27°C wires were in use for an average of 66 days.

One-way ANOVA comparisons of the 27°C, 35°C, and 40°C wires in as-received condition revealed significant differences ($P < .05$) in heating onset, endset, and enthalpy and cooling onset, endset, and enthalpy. Post hoc Tukey tests revealed the individual differences, as shown in Tables 1 and 2. A paired *t*-test showed no significant difference ($P > .05$) in as-received and retrieved 35°C archwires for all parameters. The 27°C wires exhibited a significant ($P = .04$) decrease in enthalpy associated with the heating endothermic peak in comparing the clinically retrieved wires with the as-received wires. Otherwise, all other parameters were not significantly different ($P > .05$) between as-received and retrieved 27°C wires.

DISCUSSION

The three CuNiTi archwires with different transformation temperatures are marketed to provide differing force levels depending upon the temperature of the oral environment. Correspondingly, they might be of greater use for different types of orthodontic patients.[27] The A_f of the 27°C and 35°C CuNiTi wires in this study were within approximately 2°C of the manufacturer's claim, similar to that found in other studies.[17,26] The larger standard deviation in A_f with the 27°C and 35°C varieties compared with the 40°C wires may be attributed to the presence of R-phase observed in some but not all wires tested in each group, as discussed below. In contrast to the other temperature variants, the 40°C wires displayed A_f (36.3 ± 0.6°C) below those claimed by the manufacturer, with the disparity between measured and claimed A_f being the greatest in this group. The transformation temperature in this study is comparable with the A_f of 37°C by Iijima et al[5] but not with the value of 41.2°C found by McCoy.[26] A possible cause of the discrepancy among studies might be due to variability within the lots tested, as heat treatment, amount of cold working, Ni:Ti ratio, and other manufacturing variables have been found to alter transformation temperatures.[28,29]

A lower-than-expected A_f for the 40°C CuNiTi wires may have some clinical implications. Iijima et al[5] showed that force values of various NiTi wires, includ-

Table 1. Differential scanning calorimetry–measured temperature and enthalpy changes for phase transformations during heating of copper-nickel-titanium (CuNiTi) wires[a]

CuNiTi variety, °C	Condition	Days in clinical service	Heating onset, °C		Heating endset, °C		Heating enthalpy, J/g	
27	As-received	N/A	3.2 ± 4.0	A	29.2 ± 5.4	A	−14.7 ± 0.6	A*
27	Retrieved	66 ± 16	3.2 ± 3.1		29.1 ± 5.7		−13.5 ± 1.6	*
35	As-received	N/A	10.6 ± 4.0	B	36.0 ± 3.4	B	−14.5 ± 1.2	A
35	Retrieved	47 ± 20	12.1 ± 5.8		35.9 ± 3.3		−14.6 ± 1.6	
40	As-received	N/A	18.1 ± 1.5	C	36.3 ± 0.6	B	−16.3 ± 0.6	B

[a] For as-received wires, measures with the same letter were not significantly different (analysis of variance and post hoc Tukey; $P > .05$). N/A indicates not applicable.

* Denotes a paired *t*-test showed a significant difference ($P < .05$) between as-received and retrieved wires within a single-temperature variety of CuNiTi wires (27°C or 35°C).

Table 2. Differential scanning calorimetry–measured temperature and enthalpy changes for phase transformations during cooling of copper-nickel-titanium (CuNiTi) wires[a]

CuNiTi variety, °C	Condition	Days in clinical service	Cooling onset, °C		Cooling endset, °C		Cooling enthalpy, J/g	
27	As-received	N/A	8.5 ± 2.1	A	−20.6 ± 5.5	A	13.7 ± 1.3	A
27	Retrieved	66 ± 16	9.0 ± 2.1		−21.9 ± 5.8		13.6 ± 1.6	
35	As-received	N/A	11.4 ± 1.4	B	−10.1 ± 3.7	B	14.9 ± 1.4	A
35	Retrieved	47 ± 20	12.3 ± 0.9		−8.7 ± 5.7		14.9 ± 2.4	
40	As-received	N/A	12.2 ± 0.9	B	−2.7 ± 2.3	C	17.3 ± 0.6	B

[a] For as-received wires, measures with the same letter were not significantly different (analysis of variance and post hoc Tukey; $P > .05$). A paired *t*-test showed no significant difference between as-received and retrieved wires within a single-temperature variety of CuNiTi wires (27°C or 35°C). N/A indicates not applicable.

ing 40°C CuNiTi, vary with temperature and A_f. Sakima et al[2] similarly showed progressively greater forces delivered as temperature increased from 30°C to 40°C. Because of the low A_f found in this study, the 40°C CuNiTi wires may not be delivering forces intermittently as advertised or as light of forces, and this could affect the treatment outcome.

Qualitative examination of the DSC thermograms showed the rhombohedral or R-phase that has been observed in other NiTi studies[15,16,26,30] was also found in this study. The R-phase was detected in all 40°C heating peaks, all but one set of the 35°C heating peaks, and two of six 27°C heating peaks. McCoy[26] observed the R-phase to be present in 35°C and 40°C wires but not in 27°C CuNiTi wires. However, other studies in which DSC was performed on 35°C or 40°C wires found no R-phase by conventional DSC techniques.[5,17] The work of Brantley et al[16] consistently observed the R-phase in both the heating and cooling curves when the nonreversing component of temperature-modulated DSC (TM-DSC) was plotted.

Temperature-modulated DSC utilizes a sinusoidal temperature waveform that is superimposed upon the linear heating or cooling rate typical of conventional DSC. Consequently, TM-DSC may provide greater resolution and separation of complex transitions into components. It is possible that the R-phase exists in both the heating and cooling of all three wire types studied, but the R-phase peak is sometimes imperceptibly small and would be seen only if temperature-modulated DSC were used.[16] Similarly, Brantley et al[16] observed low-temperature, nonreversing component peaks attributed to transformations within the martensitic structure of NiTi and CuNiTi wires by TM-DSC that were not observed in this study by conventional DSC. Variability within the manufacturing process, as mentioned above, may be the reason why the R-phase appears in some, but not all, specimens of a given temperature variant in this study by conventional DSC. Most likely, these same factors make it more probable for the R-phase to appear in the higher-A_f CuNiTi wires.

Comparison of DSC parameters for as-received and clinically retrieved 35°C CuNiTi wires showed no differences. Similar results were obtained for all the DSC parameters for the 27°C CuNiTi wires, except for a significant decrease in enthalpy after use for the martensite-to-austenite transition. Several possible explanations exist for this difference. Because the 27°C wires can take greater force to engage in the mouth because of their being austenite well below oral temperatures, the presence of latent martensite formed with deformation cannot be ruled out. However, because strains up to 10% have been observed to be necessary to cause residual martensite in superelastic NiTi,[31] coupled with the fact that the tested wires showed no signs of permanent deformation and the test segments were obtained from relatively straight segments of the arch that correspond to areas that do not experience substantial stress during clinical use, this explanation may be unlikely. Furthermore, Brantley et al[16] showed that laboratory bending to 135° for one superelastic, nonshape-memory wire and two superelastic, shape-memory wires had little effect on the reversing curves (as displayed in conventional DSC) generated by temperature-modulated DSC. Other factors experienced in the oral cavity (eg, temperature cycling; corrosion; and exposure to electrolytes, proteins, and fluoride) conceivably could play a role in the observed decrease in enthalpy of the transformation after clinical use. Further study of this result and the factors mentioned, as well as elucidating why the 27°C and not the 35°C wires were affected, appears warranted.

A decrease in the transformation enthalpy with clinical use would indicate a lessening of the extent of phase transformation. Although statistically significant, the clinical significance of this reduction in enthalpy is not known at this time. Other studies have observed NiTi properties to be affected after clinical use.[24,25] On the basis of temperature-modulated DSC curves showing substantial nonreversing phenomena, Brantley et al[16] speculated that some transformations in NiTi wires may not be completely reversible on the atomic level, possibly leading to structural defects and decreased clinical performance. Further research is needed to resolve the significance and speculation associated with these observations.

CONCLUSIONS

- The A_f of 27°C and 35°C CuNiTi archwires were within approximately 2°C of those claimed by the manufacturer.
- The A_f of 40°C CuNiTi archwires were 3.6°C lower than those claimed by the manufacturer. Clinical implications may be greater than expected forces and more constant, rather than intermittent, forces when these wires are used.
- Comparison of measured DSC parameters showed no difference between as-received and clinically retrieved wires, except for a significant reduction in heating enthalpy associated with the martensite-to-austenite transition in the 27°C CuNiTi archwires.

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