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-
temperature 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 (\(\Delta H\)) of the phase transformation, and austenitic finish temperature (\(A_f\)) of the endothermic peak. The cooling equivalents are the martensitic start temperature (\(M_s\)), \(\Delta H\) 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 NiTi 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.

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, 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. \(\Delta H\), 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
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 CuNiTi wires had two overlapping peaks corresponding to the R-phase transition (smaller peak on the shoulder of the previous) and the R-phase-to-austenite transition (larger peak). 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. Differential scanning calorimetry–measured temperature and enthalpy changes for phase transformations during heating of copper-nickel-titanium (CuNiTi) wires

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

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).

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 Af 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 Af 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 Af (36.3 ± 0.6°C) below those claimed by the manufacturer, with the disparity between measured and claimed Af being the greatest in this group. The transformation temperature in this study is comparable with the Af of 37°C by Iijima et al5 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 Af for the 40°C CuNiTi wires may have some clinical implications. Iijima et al5 showed that force values of various NiTi wires, includ-
Table 2. Differential scanning calorimetry–measured temperature and enthalpy changes for phase transformations during cooling of copper-nickel-titanium (CuNiTi) wires*

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

* 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 A5, Sakima et al15 similarly showed progressively greater forces delivered as temperature increased from 30°C to 40°C. Because of the low A5 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 studies15,16,26,30 was also found in this study. The R-phase was detected in all 40°C CuNiTi wires, except for a CuNiTi wires showed no difference in enthalpy after use for the martensite-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 the R-phase, 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 did not experience substantial stress during clinical use, this explanation may be unlikely. Furthermore, Brantley et al16 showed that laboratory bending to 135° for one superelastic, nonshape-memory wire and two superelastic, shape-memory wires allowed the presence of latent martensite to be observed during the cooling of the transformation after clinical use. Further study of this result and the factors mentioned, as well as elucidating why the 27°C wires 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 al16 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.

REFERENCES