Metallurgical Characterization of Controlled Memory Wire Nickel-Titanium Rotary Instruments

Ya Shen, DDS, PhD,* Hui-min Zhou, PhD,† Yu-feng Zheng, PhD,‡ Les Campbell, DDS,* Bin Peng, DDS, PhD,§ and Markus Haapasalo, DDS, PhD*

Abstract

Introduction: To improve the fracture resistance of nickel-titanium (NiTi) files, manufacturers have introduced new alloys and developed new manufacturing processes for the fabrication of NiTi files. This study aimed to examine the phase transformation behavior and microstructure of NiTi instruments from a novel controlled memory NiTi wire (CM wire). Methods: Instruments of EndoSequence (ES), ProFile (PF), ProFile Vortex (Vortex), Twisted Files (TF), Typhoon (TYP), and Typhoon™ CM (TYP CM) were examined by differential scanning calorimetry (DSC) and x-ray diffraction (XRD). Microstructures of etched instruments were observed by optical microscopy and scanning electron microscopy with x-ray energy-dispersive spectrometric (EDS) analyses. Results: The DSC analyses showed that all NiTi instruments had an austenite transformation completion temperature exceeding 37°C, whereas the NiTi instruments made from conventional superelastic NiTi wire (ES, PF, and TYP) and TF had temperatures substantially below mouth temperature. The higher austenite temperature of TYP CM instruments was consistent with a mixture of austenite and martensite structure, which was observed at room temperature with XRD. All NiTi instruments had room temperature martensite microstructures consisting of colonies of lenticular features with substantial twinning. EDS analysis indicated that the precipitates in all NiTi instruments were titanium-rich, with an approximate composition of T12Ni. Conclusions: The TYP CM and Vortex instruments with heat treatment contribute to increase austenite transformation temperature. The CM instrument has significant changes in the phase transformation behavior, compared with conventional superelastic NiTi instruments. (J Endod 2011;37:1566–1571)

Key Words

Calorimetry, controlled memory, differential scanning, microstructure, nickel-titanium instrument, phase transformation

The nickel-titanium (NiTi) alloy, which consists of nickel and titanium in a nearly equal atomic ratio, possesses unique mechanical properties. These include a shape-memory effect and superelasticity characteristics (1). Nickel-titanium alloy is able to undergo a nondiffusive transformation of the lattice structure into a martensitic phase when suitably stressed. Such stress-induced martensitic (SIM) transformation is reversible, and hence the material exhibits an unusually large elastic range and is able to recover from a much higher strain than stainless steel can withstand without breaking. This special mechanical property is called superelasticity (2–4). The critical stress for SIM transformation is governed by the heat treatment and the amount of cold work of the material (5); it changes as the material work-hardens on repeated loading (6). This reversible thermoelastic martensitic transformation is the main reason for increased flexibility of NiTi instruments over traditional stainless steel ones, which facilitates instrumentation of curved root canals (7, 8). On the other hand, separation (fracture) of NiTi instruments can still occur as a result of (1) rotational bending, ie, as a result of fatigue, or (2) shear fracture, usually when the instrument tip is stalled (jammed) but the handpiece continues to rotate (9–11). Fatigue has been implicated to be one of the main reasons for the fracture of endodontic rotary files used clinically (10, 12).

Several strategies have been used to improve the fatigue resistance of NiTi endodontic instruments. These strategies include electropolishing, ion implantation, surface coatings, and heat treatment. Recently, thermal treatment of NiTi alloy has been used to optimize the mechanical properties of this alloy (13–15). NiTi rotary instruments (Typhoon™ CM; clinician’s Choice Dental Products, New Milford, CT) made from a NiTi wire subjected to proprietary thermomechanical processing (CM Wire) have been introduced into the market. One study (16) showed that these instruments have superior fatigue resistance than conventional NiTi rotary instruments made from superelastic wire. However, the fundamental mechanism for this improved performance is unknown. Because the microstructure and phase transformation behavior determine the mechanical properties of NiTi alloys, the study of the phase transformations could provide significant information for the new CM Wire instruments. Therefore, the hypotheses for this research project were that the thermomechanical processing used for CM Wire that is machined into rotary Typhoon CM endodontic instruments...
results in significant changes in the microstructure and phase transformation behavior, compared with conventional superelastic NiTi instruments.

Materials and Methods

Differential Scanning Calorimetry

Instruments of EndoSequence (ES) (lot 15426; Brasseler USA, Savannah, GA), ProFile (PF) (lot 061608534; Dentsply Maillefer, Ballaigues, Switzerland), ProFile Vortex (Vortex) (lot 052709555; Dentsply Tulsa Dental Specialties, Tulsa, OK), Twisted Files (TF) (lot 021004339; SybronEndo, Orange, CA), Typhoon (TYP) (lot 040510002; Clinician’s Choice Dental Products), and Typhoon™ CM (TYP CM) (lot 04051003; Clinician’s Choice Dental Products), all size 25/.04, were evaluated. Test specimens were carefully cut from each instrument by using a water-cooled, slow-speed diamond saw. Each test specimen for differential scanning calorimetry (DSC) analysis consisted of 1–2 segments, each approximately 4–5 mm in length, that were from adjacent portions of the shaft. Five specimens for each group were subjected to the test. Each test specimen was placed in an open aluminum pan; no crimped pan top was used to avoid mechanical stresses on the specimens. An empty aluminum pan served as the inert control specimen for the DSC measurements.

The DSC analyses were conducted (PYRIS, Perkin Elmer Diamond Series DSC; PerkinElmer, Shelton, CT) over a temperature ranging from −100°C to 100°C by using the liquid nitrogen cooling accessory to achieve subambient temperatures. For each analysis, the specimen was first heated from room temperature to 100°C, then cooled from 100°C to −100°C to obtain the cooling DSC curve, and subsequently heated from −100°C back to 100°C to obtain the heating DSC curve.

Figure 1. DSC curves of the test specimens. Heating (upper) and cooling (lower) curves are shown.
The linear heating or cooling rate was a standard 10°C/min (17, 18), and during each analysis the DSC cell was purged with dry nitrogen at a rate of 50 mL/min. Temperature calibration of the DSC apparatus was performed with indium under the experimental conditions. The plots were analyzed by PYRIS computer software (PerkinElmer Inc) to obtain the onset temperatures for the phase transformations, along with the enthalpy changes (ΔH) associated with these processes. The transformation temperatures were obtained from the intersection between extrapolation of the baseline and maximum gradient line of the lambda-type DSC curve (14, 19). The martensitic transformation-starting and transformation-finishing points (Ms, Mf) and reverse transformation-starting and transformation-finishing points (As, Af) were determined.

X-Ray Diffraction
X-ray diffraction (XRD) (X’Pert PRO; PANalytical BV, Almelo, The Netherlands) was performed (18, 20, 21) to identify phases in the wires and complement the DSC results. Analyses were performed on 5 samples each at room temperature (25°C), with CuKα monochromatic radiation at 40 kV and tube current of 100 mA. Segments from the shank portions of NiTi instruments were cut from the file by using a low-speed, water-cooled diamond saw, and then multiple segments were adhered together and ground by using 2000# SiC sandpaper to obtain a plane. Then the segments were cleaned by acetone and distilled water and placed side by side on the glass sample holder. The peaks were identified by using the pattern library Powder Diffraction File (PDF release 2004; International Centre for Diffraction Data, Newtown Square, PA) by the software MDI Jade5.0 (Materials Data, Inc, Livermore, CA).

The plots were analyzed by PYRIS computer software (PerkinElmer Inc) to obtain the onset temperatures for the phase transformations, along with the enthalpy changes (ΔH) associated with these processes. The transformation temperatures were obtained from the intersection between extrapolation of the baseline and maximum gradient line of the lambda-type DSC curve (14, 19). The martensitic transformation-starting and transformation-finishing points (Ms, Mf) and reverse transformation-starting and transformation-finishing points (As, Af) were determined.

**X-Ray Diffraction**

X-ray diffraction (XRD) (X’Pert PRO; PANalytical BV, Almelo, The Netherlands) was performed (18, 20, 21) to identify phases in the wires and complement the DSC results. Analyses were performed on 5 samples each at room temperature (25°C), with CuKα monochromatic radiation at 40 kV and tube current of 100 mA. Segments from the shank portions of NiTi instruments were cut from the file by using a low-speed, water-cooled diamond saw, and then multiple segments were adhered together and ground by using 2000# SiC sandpaper to obtain a plane. Then the segments were cleaned by acetone and distilled water and placed side by side on the glass sample holder. The peaks were identified by using the pattern library Powder Diffraction File (PDF release 2004; International Centre for Diffraction Data, Newtown Square, PA) by the software MDI Jade5.0 (Materials Data, Inc, Livermore, CA).

**Figure 2.** XRD patterns for NiTi instruments at 25°C.
Microstructures of Etched Specimens

The files were cut into 5-mm segments. Specimens were embedded in acrylic resin to reveal the horizontal surface along the axis. All specimens were polished with a standard sequence of metallocraphic abrasives. The polished surfaces were etched in a solution (3 mL hydrofluoric acid, 5 mL nitric acid, and 20 mL acetic acid) that revealed detailed microstructures. The etched microstructures of instrument specimens were examined with an inverted optical microscope (Axiovert 200MAT; Carl Zeiss MicroImaging, Inc, Göttingen, Germany) and scanning electron microscopy (SEM) (QUANTA 200; FEI Company, Hillsboro, OR). The compositions of precipitates in the microstructures were obtained by energy-dispersive spectrometric analyses (EDS) (Oxford Instrument, Oxfordshire, UK) with the SEM.

Results

Figure 1 presents DSC plots for both the heating and cooling cycles of different types of instruments. In all of the DSC plots, the heating curve is shown at the top of the figure, and the cooling curve is shown at the bottom of the figure. The typical DSC curve for conventional superelastic rotary instruments (eg, ES file in Fig. 1B) exhibited single and defined peak on cooling and heating, respectively. This represents the martensitic and reverse transformation between austenite and martensite. The $\Delta T$ temperatures for conventional superelastic rotary instruments (ES, PF, and TYP files) and TF instruments were lower than the body temperature of 37°C (Fig. 1 and Table 1). Two endothermal peaks were observed on the heating curve of TF files; the first peak corresponded to the initial transformation from martensite to R-phase, and the second peak corresponded to the transformation from R-phase to austenite; the transformation to austenitic NiTi on heating ($A_f$ temperature) was completed at approximately 18°C (Fig. 1C and Table 1); the single peak on the cooling cycle corresponded to the transformation from austenite to martensite. Although only single and defined peak on cooling and heating was detected in Vortex file (Fig. 1D), approximate $A_f$ temperature was 50°C (Table 1). For this specimen, the enthalpy value of 5.7 J/g was applicable to the overall transformation from martensitic NiTi to austenitic NiTi when the sample was heated. For TYP CM instrument, a double endothermic peak on the heating (upper) curve represented the transformation from martensite to R-phase, followed by transformation from R-phase to austenite phase. The austenite-finish transformation temperature was 54°C, and enthalpy change was 19.9 J/g (Fig. 1F and Table 1); the 3 peaks on the cooling cycle of TYP CM files indicated 3-stage phase transformation. The DSC plots of the other 4 instruments in each group were very similar.

XRD patterns at 25°C in ES, PF, TF, Vortex, and TYP files for diffraction angles (2θ), ranging from 20° to 100°, contained 3 major peaks for the (110), (200), and (211) atomic planes in austenite (Fig. 2). The major peak for the (200) austenite atomic plane was weak. For TYP CM instruments, XRD pattern contained numerous peaks that could be indexed to atomic planes of martensite.

Optical microscope images of all etched instruments exhibited the classic lenticular martensite structure with substantial twinning (Fig. 3). Inclusions randomly distributed in the matrix of the NiTi alloy of all instruments were examined (Fig. 3A). All instruments showed much the same size and density of inclusions. The EDS analysis conducted on the inclusions was titanium-rich, with an approximate composition of Ti$_2$Ni. The NiTi matrix confirmed a composition of roughly 55% Ni and 45% Ti. The EDS analysis indicated that all instruments had near equiatomic NiTi compositions. The precipitates were titanium-rich, with an approximate composition of Ti$_2$Ni.

Discussion

In the present study, various metallurgical laboratory techniques (DSC, XRD, optical microscope, SEM, and EDS) were used to investigate the microstructure and phase transformations of rotary endodontic instruments made from different types of NiTi wires. Although XRD analysis is a useful method to investigate the structure of NiTi phases at specific positions (21), this technique only reveals the structure within approximately 50 µm of the surface, whereas DSC as a complementary analytical technique provides information for the overall bulk specimen and the effects of temperature changes on the phase transformations (15, 17, 18, 22). Microstructural features in most materials must be revealed by etching the sample. Etching can modify the composition of a specimen in the critical near-surface region. Furthermore, it can reveal the different microstructural features that vary from area to area. The surface corrodes selectively as a consequence of different grain orientations, crystal defects such as dislocations and grain boundaries, cold worked regions, and second phases. The TF with R-phase technology and ProFile Vortex and Typhoon CM were evaluated compared with conventional superelastic rotary instruments in this study.

The DSC results showed that the TYP CM and Vortex instruments had an $A_f$ temperature exceeding 37°C, whereas the NiTi instruments made from conventional superelastic NiTi wire (ES, PF, and TYP) and TF instrument had $A_f$ temperatures substantially below mouth temperature (from 16°C–31°C). Those data are in accordance with previous studies that found that the conventional superelastic NiTi file...
Basic Research—Technology

has an austenite structure (14, 17, 18, 22), whereas NiTi file with thermal processing (eg, Vortex) would be essentially in the martensitic condition at body temperature (14, 15, 22). The martensitic phase of NiTi has some unique properties that have made it an ideal material for many applications (23). The martensitic phase transformation has excellent damping characteristics because of the energy absorption characteristics of its twinned phase structure. In addition, the martensitic form of NiTi has remarkable fatigue resistance. The instruments of martensite phase can be easily deformed, yet they will recover their shape on heating above the transformation temperatures. The bulk material properties are the main determinant of fatigue life (13, 24, 25). Gao et al (25) found that Vortex instruments exhibited superior cyclic fatigue resistance compared with those made of regular superelastic NiTi files. Current study showed that TYP CM file was >300% more resistant to fatigue failure than TYP instrument (16). Although the thermomechanical treatment history for the TYP CM file made from CM Wire and Vortex made from M-wire is not clear, it seems that thermomechanical processing is a very promising way to increase the fatigue resistance of NiTi endodontic instruments.

The mechanical behavior of NiTi alloy is determined by the relative proportions and characteristics of the 3 NiTi microstructural phases: martensite, austenite, and R-phase. Heat treatment or thermal processing is one of the most fundamental approaches to adjust the transition temperature in NiTi alloy, which might increase the fatigue resistance of NiTi endodontic files. Alapati et al (22) found that heat treatments at 400°C, 500°C, and 600°C raised the A_f temperature of ProFile to 45°C–50°C, and heat treatment at 850°C caused drastic changes in transformation behavior; the DSC curves were very complex with irregular peaks. Other studies had also reported that heat treatment at temperatures higher than 600°C would cause recrystallization of the microstructure, which should be avoided for rotary instruments (26, 27). Thermomechanical processing is a complicated process, which integrates the work hardening and heat treatment into a single process. The manufacturer must perform an appropriate heat treatment, which will be accompanied by beneficial changes in mechanical properties and improved clinical performance.

Various methods have been suggested to change the mechanical properties of the NiTi alloy used for rotary instruments. Twisted File is fabricated as transforming basic austenite NiTi wire into the R-phase through a thermal process. After the twisted shape is achieved, a series of heating and cooling cycles are said to convert the twisted R-phase wire back to the austenite crystalline structure, which becomes superelastic while stressed (28). Although TF files consist mainly of austenite in the oral environment, the bending load values in elastic and superelastic ranges were lower for TF than those of conventional superelastic NiTi file (19). This is not surprising because the 2-step transformation through an apparent R-phase was observed for TF in our DSC results (Fig. 1C). R-phase possesses lower shear modulus than martensite and austenite, and the transformation strain for R-phase transformation is less than one-tenth of that of martensitic transformation (29). More research is needed to identify the effect of heat treatment on NiTi instrument related to cutting efficiency and surface hardness.

Although the A_f temperature of Vortex instruments was up to 50°C, the martensite condition existed at room temperature. However, the result from XRD showed that there were the relative intensities of the austenite peak in Vortex instrument at room temperature. The enthalpy change during the DSC measurement for Vortex files (5.7 J/g) was much lower than that for superelastic orthodontic wires (usually above 10 J/g) (30), suggesting that the amount of martensite participating in the phase transformation was relatively low. Note that for the TYP CM case, enthalpy change for transformation was more than 19 J/g. XRD found that TYP CM files contained martensite and austenite at room temperature. The different A_f temperatures and the enthalpy change values for TYP CM and Vortex instruments contributed to this phenomenon. In addition, etched NiTi instruments had classic lenticular martensitic microstructures when viewed with the optical microscope at room temperature. These observations were in agreement with results from our DSC study, which suggested that TYP CM instrument was martensite and austenite at room temperature. The unexpected observation was that at room temperature the conventional superelastic NiTi instruments had a similar, largely martensitic microstructure, although DSC analyses indicated that the conventional NiTi instrument had an austenitic microstructure. It might be possible that the DSC detects only the martensite that transforms to austenite and not stabilized martensite that does not undergo transformation. These data are in accordance with previous studies (15, 22) that found that both heat treatment NiTi instruments and conventional superelastic NiTi instruments contain substantial amounts of martensite that do not undergo transformation.

Within the limitations of this study, TYP CM and Vortex instruments had an A_f temperature exceeding 37°C, whereas the NiTi instruments made from conventional superelastic NiTi wire (ES, PF, and TYP) and TF had A_f temperatures substantially below mouth temperature. The higher A_f temperature of TYP CM instruments was consistent with a mixture of austenite and martensite structure, which was observed at room temperature with XRD. All NiTi instruments had room temperature martensite microstructures consisting of colonies of lenticular features with substantial twinning.

Acknowledgments

The authors thank Dentsply Tulsa Dental Specialties and Clinician’s Choice Dental Products for donating the files used in this study.

The authors deny any conflicts of interest related to this study.

References