AN INVESTIGATION OF PHASE TRANSFORMATION MECHANISMS FOR NICKEL-TITANIUM ROTARY ENDODONTIC INSTRUMENTS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for

the Degree Doctor of Philosophy in the

Graduate School of The Ohio State University

By

Satish B. Alapati, BDS, MS

* * * * *

The Ohio State University

2006

Dissertation Committee

Dr. William A. Brantley, Adviser

Dr. John M. Nusstein

Dr. William M. Johnston

Approved by

____

Adviser

College of Dentistry

ABSTRACT

The concern of nickel-titanium instrument separation is still a challenge confronting every manufacturer and endodontist, and such separation often seems to happen without any prior signs of permanent deformation. Nickel-titanium instruments based upon the equiatomic intermetallic compound NiTi have gained considerable popularity among endodontists because of their very low modulus of elasticity, which enables these instruments to negotiate curved root canals during conventional root canal therapy. NiTi exists in two major microstructural phases: austenite, the high-temperature and low-stress form, and martensite, the low-temperature and high-stress form. An intermediate R–phase is also sometimes observed for the transformation between austenite and martensite. The structural transformations in NiTi occur rapidly by twinning on the atomic level and are reversible for stresses below the onset of permanent deformation.

The nickel-titanium rotary instruments are intentionally manufactured in the superelastic condition, which provides the capability of extensive elastic strain without fracture under clinical conditions associated with root canal therapy. The microstructural phases present in the NiTi rotary instruments were studied by Micro x-ray diffraction (Micro-XRD) and temperature-modulated differential scanning calorimetry (TMDSC). The latter analytical technique provided information about the variations in proportions of the phases with temperature.

The overall objective of this study was to gain new insight into the microstructural phases and their transformations that would provide the basis for improved clinical performance of NiTi rotary instruments. The phases present were identified by Micro-XRD and TMDSC, using the clinically popular ProFile GT and ProTaper nickel-titanium rotary instruments, which have two different cross-sectional designs. Instruments were analyzed in the as-received condition and after clinical use, as well as following elevated-temperature heat treatments. The *first* null hypothesis for this research was that microstructural phases and phase transformations do not have an impact on clinical performance and instrument failure. The *second* null hypothesis was that appropriate heat treatments previously used for orthodontic wires will not result in beneficial changes in microstructural phases that may significantly affect the clinical life of these instruments. Based upon this research and complimentary previous studies by this investigator, both null hypotheses were rejected. Information obtained from this research should be of importance for the future development of improved instruments with reduced likelihood of failure during clinical use.

DEDICATION

This study is dedicated to my family, parents and friends who have provided me unwavering love, support, and motivation throughout my life.

ACKNOWLEDGMENTS

I would like to express sincere appreciation to my advisor, Dr. William A. Brantley, for the ubiquitous role he has had in all aspects of my academic program and dissertation work. I would also like to thank Dr. John M Nusstein and Dr. William Johnston, for their unswerving willingness to actively participate in my committee and also for their encouragement and challenge throughout my academic program. I am also highly appreciative to Dr. Rudy Melfi for expert advice on dental hard tissues and pulp biology. I am also highly appreciative to Dr. Robert Seghi and to the entire faculty in the Section of Restorative and Prosthetic Dentistry for their support throughout my academic program. My sincere appreciation goes to Dr. Glenn Daehn in the Department of Materials Science and Engineering for his valuable guidance and motivation over the years. It is highly important for me to acknowledge my early mentor at the Northwestern University Dental School, Dr. James Bahcall, who constantly provided me great moral support when I needed it the most at very early stages. Lastly, sincere thanks to Dr. Scott Schricker for allowing me use of his laboratory facilities to perform the Temperature-Modulated Differential Scanning Calorimetric experiments and to Dr. Masahiro Iijima at the Hokkaido Health Sciences University in Japan for performing the Micro-X-Ray Diffraction experiments.

VITA

September, 1972....................................Born, Andhra Pradesh, INDIA

March, 1996.......................................Bachelor of Dental Surgery, Bapuji Dental College and Hospital, Kuvempu University, Davangere, Karnataka, INDIA

1997-1998..General Practice Residency, Truman Medical Center, University of Missouri-Kansas City.

2003..M.S., Dental Materials, Ohio State University

2001-present.......................................Graduate Teaching/Research Assistant, Section of Restorative and Prosthetic Dentistry, College of Dentistry, The Ohio State University

PUBLISHED ABSTRACTS AND PUBLICATIONS

1. SEM Observations of New and Used Nickel-Titanium Rotary Files. Alapati S, Brantley WA, Mitchell JC, Iijima M, Svec TA, Powers JM. J Dent Res 2002; 81 (Special Issue A): Abstract No. 3859 (www.dentalresearch.org).

2. Fatigue Limits and SEM/TEM of Fracture Characteristics for Pd-Ag Alloys. Li D, Brantley WA, Guo WH, Clark WAT, Alapati S, Heshmati RH, Daehn GS. J Dent Res 2003; 82 (Special Issue A): Abstract No. 128 (www.dentalresearch.org).

3. SEM Observation of Deformed and Fractured Nickel-Titanium Rotary Endodontic Instruments. Svec TA, Alapati S, Brantley WA, Powers JM, Nusstein JM. J Dent Res 2003; 82 (Special Issue A): Abstract No. 1528, (www.dentalresearch.org).

4. Vickers Hardness Investigation of Work-Hardening in Used Nickel-Titanium Rotary Instruments. Alapati S, Brantley WA, Guo WH, Svec TA, Powers JM, Nusstein JM. J Dent Res 2003; 82 (Special Issue A): Abstract No. 1529 (www.dentalresearch.org).

5. Fracture Toughness and SEM Evaluation of Fiber-reinforced Provisional Restoration Resin. Hamza TA, Rosenstiel SF, Alapati SB, EL-Hosary MM, Ibraheem RM; J Dent Res 83 (Special Issue A): Abstract No. 409, 2004 (www.dentalresearch.org).

6. Contact Angles of Orthodontic Elastomeric Chains in Two Media. Webb CS, Alapati S, Johnston W, Brantley WA, Vig KWL, Liu R. J Dent Res 2004; 83 (Special Issue A): Abstract No. 1387 (www.dentalresearch.org).

7. Fatigue of Two Pd–Ag Alloys and SEM of Fracture Surfaces. Li D, Baba N, Alapati S, Heshmati R, Brantley WA. J Dent Res 2004; 83 (Special Issue A): Abstract No.2685 (www.dentalresearch.org).

8. SEM Observations of RaCe Rotary Instruments after Simulated Clinical Use. Sanli Y, Alapati SB, Nusstein JM, Brantley WA, Baba N, Svec T, Powers JM. J Dent Res 2004; 83 (Special Issue A): Abstract No. 2686 (www.dentalresearch.org).

9. SEM Microstructural Observations and Vickers Hardness Measurements for Pd-Ag Alloys. Baba N, Li D, Alapati S, Heshmati R, Brantley WA. J Dent Res 2004; 83 (Special Issue A): Abstract No.3976 (www.dentalresearch.org).

10. Fractographic Studies of Nickel-Titanium Rotary Instruments. Svec TA, Brantley WA, Alapati SB, Daehn GS, Nusstein JM, Powers JM. J Endod 2004; 30: 272 (Abstract No.69).

11. Vickers Hardness Measurements and Microstructural Observations of Soldered Beta-Titanium Wires. Baba N, Alapati SB, Iijima M, Brantley WA, Kawashima I, Ohno H, Mizoguchi I. J Dent Res 84 (Special Issue A): Abstract No. 646, 2005 (www.dentalresearch.org).

12. Microstructure, Chemical Composition and Vickers Hardness of Straumann Implant Component. Sanli Y, Baba N, Alapati SB, Li D, Brantley WA. J Dent Res 2005; 84 (Special Issue A): Abstract No. 1417 (www.dentalresearch.org).

13. SEM and EPMA Investigation of Soldered Beta-Titanium Orthodontic Wires. Iijima M, Brantley WA, Kawashima I, Alapati SB, Baba N, Yuasa T, Mizoguchi I. J Dent Res 2005; 84 (Special Issue A): Abstract No 1475 (www.dentalresearch.org).

14. Micro-XRD Study of Nickel-Titanium Rotary Endodontic Instruments after Clinical Use. Iijima M, Brantley WA, Alapati SB, Nusstein JM. J Dent Res 2005; 84 (Special Issue A): Abstract No. 1479 (www.dentalresearch.org).

15. Investigation of Transformations in Used and Heat-Treated Nickel-Titanium Endodontic Instruments S.B. Alapati, W.A. Brantley, S.R. Schricker, J.M. Nusstein, U.-M. Li , and T. Svec, J Dent Res 2006; 85(Special Issue A): Abstract No.0038, 2005 (www.dentalresearch.org).

16. Micro-XRD and SEM of NiTi Instruments Modified by Ion Implantation U.-M. Li, M. Iijima, W.A. Brantley, S.B. Alapati, C.P. Lin 4, J Dent Res 2006; 85 (Special Issue A): Abstract No. 0037 (www.dentalresearch.org)

17. Casting Dimensions, Porosity and Mechanical Properties for Palladium–Silver Alloys D. Li, N. Baba, X. Hu, S.B. Alapati, W.A. Brantley, R.H. Heshmati, T. Dasgupta, P.J. McCabe, J Dent Res 2006; 85(Special Issue A): Abstract No. 1623(www.dentalresearch.org).

18. Mechanical Properties of Three Palladium-Silver Casting Alloys for Metal-Ceramic Restorations D. Li, S.B. Alapati, W.A. Brantley, W.M. Johnston, T. Dasgupta, P.J. McCabe, J Dent Res 2006; 85(Special Issue A): Abstract No.1932 (www.dentalresearch.org).

19. Effects of Porcelain-Firing and Annealing Heat Treatments on Palladium-Silver Alloys D. Li, X. Hu 1, S.B. Alapati, W.A. Brantley, R.H. Heshmati, T. Das Gupta, P.J. McCabe, J Dent Res 2006; 85(Special Issue A): Abstract No. 0039 (www.dentalresearch.org).

PUBLICATIONS

1. A review of the use of conventional DSC to study phase transformations in new and used nickel-titanium rotary endodontic instruments. Brantley W, Svec T, Iijima M, Powers J, Grentzer T, Alapati S. Proceedings of the 31st NATAS Conference, September 2003.

2. Scanning electron microscope observations of new and used nickel-titanium rotary files. Alapati SB, Brantley WA, Svec TA, Powers JM, Mitchell JC. J Endod 2003;29:667-9.

3. Proposed role of embedded dentin chips for the clinical failure of nickel-titanium rotary instruments. Alapati SB, Brantley WA, Svec TA, Powers JM, Nusstein JM, Daehn GS. J Endod 2004;30:339-41.

4. SEM observations of nickel-titanium rotary endodontic instruments that fractured during clinical use. Alapati SB, Brantley WA, Svec TA, Powers JM, Nusstein JM, Daehn GS. J Endod 2005;31:40-3.

5. The fracture toughness of denture base material reinforced with different concentrations of POSS. Hamza T, Wee AG, Alapati S, Schricker SR. J Macro Molecular Sci 2004;A41:1-10.

6. Bending fatigue study of nickel-titanium Gates Glidden drills. Leubke NH, Brantley WA, Alapati SB, Mitchell JC, Lausten LL, Daehn GS. J Endod 2005;31:523-5.

FIELDS OF STUDY

Major Field: Dentistry

Oral Biology – Biomaterials track

TABLE OF CONTENTS

Page

LIST OF TABLES

Table | Page

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Nickel-Titanium Rotary Instruments for Endodontics

Conventional endodontic treatment involves the removal of inflamed or necrotic pulp tissue from the coronal and radicular sections of the root canal, along with significant shaping of the dentin along the canal walls to facilitate better obturation. The objective is to eventually seal the apex of the root by filling the root canal with an inert material such as gutta-percha. The coronal seal is also important in the success of root canal treatment, since this is followed by placing a full coronal restoration to extend the longevity and function of the tooth in the oral cavity. The morphology of the root canal system varies from tooth to tooth and person to person (Manning, 1990a and 1990b; Sidow et al., 2000). The curvature of the root varies from 0 to 50 degrees (Cohen and Burns, 2002), and the clinician may find the negotiation of such curved canals to be both difficult and challenging.

The clinical endodontic procedure involves the sequential use of several sizes of root canal files, which are typically manufactured from stainless steel or nickel-titanium alloys. In the current practice of endodontics, engine-driven rotary instruments made of nickel-titanium alloy are widely used with a torque-control motor and handpiece. Nickel-titanium instruments were first introduced to endodontics in the landmark research by Walia et al. (1988), who investigated NiTi hand files, which are also currently marketed for clinical use. The major reason for the clinical selection of nickel-titanium instruments by endodontists is the much greater flexibility (much lower elastic modulus) of the nickel-titanium alloy compared to stainless steel (Walia et al., 1988), which offers distinct clinical advantages for shaping curved root canals.

Rotary instrument designs have changed at a rapid pace for the past two decades. In recent years there have been tremendous advances in the design of these instruments to improve the quality of root canal preparation, which leads to better obturation, apical seal, and eventually to better prognosis for the treated tooth. Nonetheless, the possibility of nickel-titanium instrument fracture is still a challenge confronting every manufacturer and practitioner who performs endodontic treatment. Despite very successful clinical performance, some incidence of nickel-titanium instrument deformation and separation seems to be inescapable, even with use of new design features and modern technology. Such instrument separation, which typically occurs without any preceding signs of permanent deformation and impending failure during root canal preparation (Patino et al., 2005, Bahia et al., 2005), is a highly unpleasant experience for the patient and the clinician.

There are several factors that contribute to fracture of the nickel-titanium rotary instruments (Bahia et al., 2005). They include the original alloy processing by the primary metals company, machining of the instrument by the file manufacturer, and mechanical properties of the nickel-titanium alloy. Another variables is manipulation of the instrument by the clinician, who must be aware of the torque delivery limits and the flexural moment produced in the root canal with a given radius of curvature. Failures of these instruments can be broadly classified into two general categories: (1) failure due to alloy properties and instrument manufacture (Kuhn and Jordan, 2002) and (2) failure due to improper manipulation by the clinician in the root canal (Cheung, 1996). Scanning electron microscope (SEM) studies of rotary instruments have revealed that surface defects, such as pitting, formation of grooves, and blunting of the cutting edges increase with clinical usage (Alapati et al., 2003).

The alloy composition used in the manufacture of nickel-titanium orthodontic wires and endodontic nickel-titanium instruments has an approximate overall composition of 55% nickel and 45% titanium (wt. %) (Thompson, 2000), and is based upon the intermetallic compound NiTi (Figure 1.1). For orthodontic purposes, the nickel-titanium alloys are marketed in superelastic, nonsuperelastic, and shape memory forms (Bradley et al., 1996; Brantley, 2001). It was reported that nonsuperelastic alloys (such as the original Nitinol from 3M Unitek) have a predominantly heavily cold-worked, stable martensitic structure, whereas the superelastic and shape memory alloys undergo reversible transformation by twinning on the atomic scale (Brantley, 2001) between the lower-temperature martensitic structure and the higher-temperature austenitic structure. The shape memory alloys return to a higher-temperature shape established during processing (Civjan et al, 1975) when the temperature is raised above the austenite-finish (A_f) temperature at which the transformation to austenitic NiTi is completed. The transformation process can be complex, with the formation of an intermediate R–phase between the martensitic and austenitic structures (Brantley, 2001). Low-temperature transformations within the martensitic NiTi structure have been reported for orthodontic nickel-titanium alloys, using electrical resistivity measurements (Chen et al., 1992) and temperature-modulated differential scanning calorimetry (TMDSC) (Brantley et al., 2002c and 2003).

The relationships between different phases in nickel-titanium alloys have been extensively studied by means of conventional differential scanning calorimetry (DSC) (Todoroki and Tamura, 1987; Yoneyama et al., 1992; Bradley et al., 1996; Brantley, 2001), which provides information about the bulk test specimen, in contrast to x-ray diffraction (Thayer et al., 1995), which only provides information about phases within less than 50 μm below the surface (Brantley, 2001). A recent review article (Thompson, 2000) has stated that the nickel-titanium rotary endodontic instruments are manufactured in the superelastic condition. This was confirmed by DSC study of two commercial products (ProFile and LightSpeed) in the as-received condition (Brantley et al., 2002a) and after simulated clinical use (Brantley et al., 2002b).

1.2 Processing of Nickel-Titanium Rotary Endodontic Instruments

Nickel-titanium endodontic instruments are machined, unlike their predecessor stainless steel root canal files, where tapered wire blanks are twisted to form the instrument. (Thompson, 2000; Cohen and Burns, 2002). The nickel-titanium rotary instruments are milled into various designs of cutting heads, flutes, shapes, tapers and sizes. Some of the newest NiTi rotary instrument products are Sequence System (VDW, Endodontic Synergy), SafeSiders (Essential Dental Systems) (Figure 1.2), Liberator (Miltex Endodontics) (Figure 1.3) and RaCe (Brasseler), all of which have unique design features. The manufacturing process for these instruments introduces a variety of defects: (1) surface flaws, such as irregularities, (2) milling marks, such as grooves, and (3) metal flash and rollover (deformation of cutting edge during manufacturing process) which are thin strips of metal at the edges of the flutes or the flat radial lands (Alapati et al., 2003). Previous investigators have considered that such defects are responsible for instrument failure during clinical use or laboratory testing (Sattapan et al., 2000; Tripi et al., 2001; Martins et al., 2002).

Some NiTi rotary instruments, such as RaCe and Sequence, are available with an electropolished surface finish. This type of surface finish reduces the extent of milling marks and metal flash, and also minimize metal rollover (Rangel et al., 2005) (Figure 1.3). Some researchers have also proposed the use of chemical vapor deposition, boron ion implantation (Lee et al., 1996), and nitrogen ion implantation (Tripi et al., 2002), with the overall objective of making the instrument surface hard and therefore improve cutting efficiency.

1.3 Nickel-Titanium (NiTi) Phases and Their Transformation Process

Rotary endodontic instruments machined from nickel-titanium alloy have considerably improved mechanical behavior compared to older stainless steel instruments because of their unique superelastic capability to develop large reversible tensile strains of about 7% – 10% (Miura et al., 1986). This superelasticity arises from the diffusion-less phase transformation by twinning between martensite and austenite phases (Wayman and Duerig, 1990; Brantley, 2001). The major phase transformation temperatures that govern the mechanical properties are termed: martensite-start temperature (M_s), martensite-finish temperature (M_f), austenite-start temperature (A_s) and austenite-finish temperature (A_f). An intermediate R–phase generally forms between martensite and austenite phases on heating and cooling for nickel-titanium orthodontic wires (Brantley et al., 2001, 2002c and 2003), so that additional R_s and R_f temperatures can be defined for the start and finish of the transformations involving R–phase.

It was previously noted in Section 1.1 that conventional DSC (Figure 1.4), temperature-modulated DSC (Figures 1.5 and 1.6), electrical resistivity measurements, and x-ray diffraction have been utilized to study phase transformations in nickel-titanium orthodontic wires. While conventional DSC is highly convenient as it provides bulk information, the present research described in later chapters employed temperature-modulated DSC, which provides detailed information about the reversing and non-reversing heat flow character of transformations in nickel-titanium rotary endodontic instruments that is not available with conventional DSC.

The thermal signatures associated with the phase transformations are exploited to determine the transformation temperatures. The calorimeter used with conventional DSC or with TMDSC monitors temperature, regulates heat flow, and records the variation of heat flow with temperature during heating and cooling. Only a very small nickel-titanium test specimen, typically 20 - 40 mg and irregular in shape, is required. A sample pan containing the test specimen cut from a nickel-titanium rotary instrument is initially cooled (along with an empty reference pan) to a sufficiently low temperature to be in the fully martensitic NiTi condition and then heated at a user-specified, computer-controlled rate. When the nickel-titanium specimen starts the initial transformation from martensite to austenite (generally involving the intermediate R–phase), it absorbs heat since this transformation is endothermic. The additional thermal energy supplied to heat the pan containing the test specimen at the same rate as the empty reference pan appears as a characteristic dip (endothermic peak) in the heating curve. Upon cooling, because the reverse transformation from austenite to martensite is exothermic, more thermal energy needs to be withdrawn from the pan containing the test specimen than from the empty reference pan to maintain the same cooling rate for both pans. A characteristic exothermic peak in the heat flow from the test specimen is observed. The starting and ending temperatures for the phase transformations are determined as the intersections of tangent lines to the peaks and adjacent baselines.

The results presented in the chapters to follow suggest that the transformation temperatures of nickel-titanium rotary endodontic instruments are affected by clinical use and heat treatment. These results may also provide a helpful reference for study of future nickel-titanium rotary endodontic instruments. The instruments are manufactured from a NiTi alloy wire in a starting cold-worked state that does not exhibit superelastic behavior, so the manufacturer must perform an appropriate proprietary heat treatment, which may also impart true shape memory at mouth temperature (below 35°C).

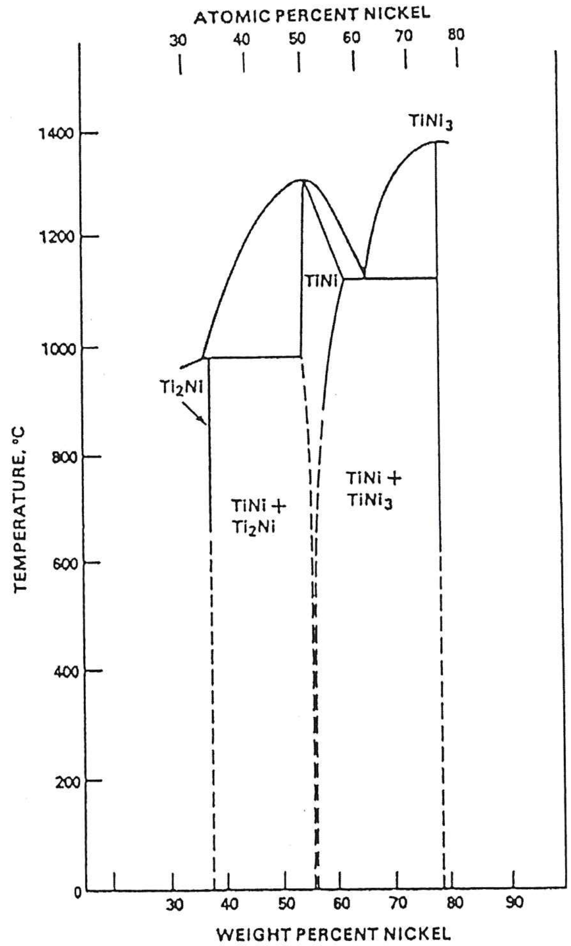

Figure 1.1: Equilibrium diagram of the nickel and titanium binary system near the NiTi phase (Brantley, 2001. Adapted from Goldstein et al., 1987).

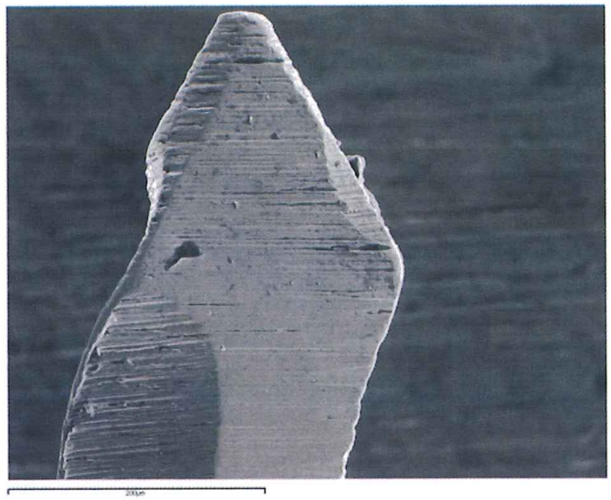

Figure 1.2: Secondary electron image of a SafeSider rotary instrument, showing flat end of a 180° cutting surface and machining marks. (Scale bar length 200 μm. Original magnification ×250)

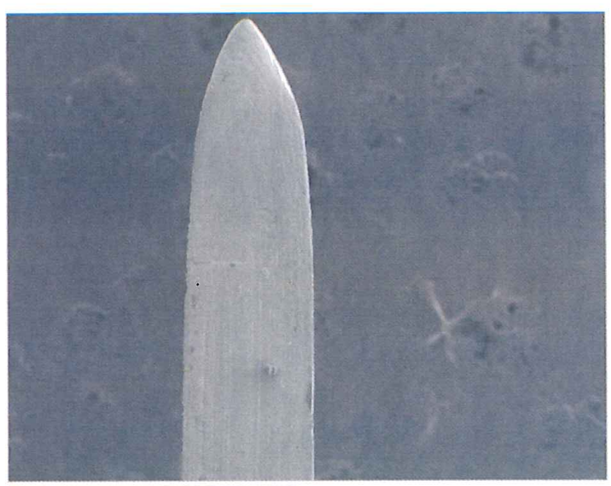

Figure 1.3: Secondary electron image of a Liberator rotary instrument, showing straight flute design. (Scale bar length 800 μm. Original magnification ×75)

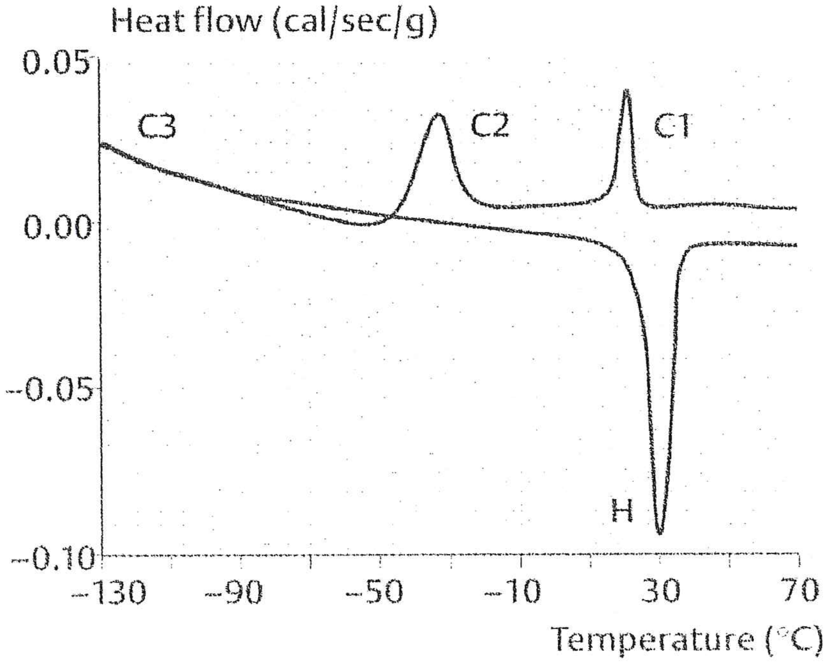

Figure 1.4: DSC heating and cooling curves for as-received Neo Sentalloy archwire segments (Brantley, 2001).

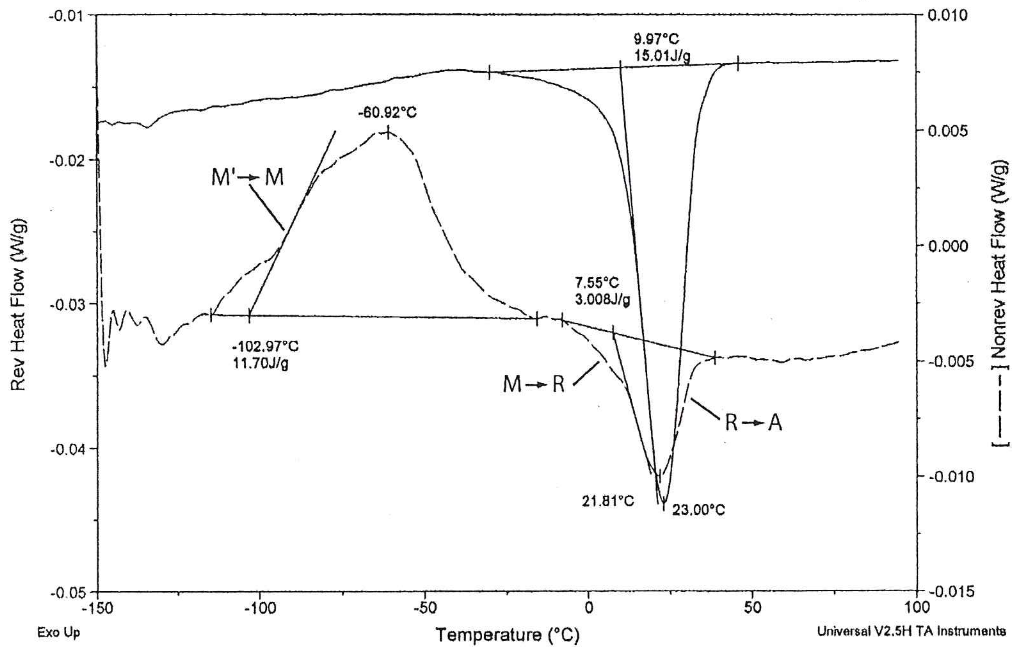

Figure 1.5: TMDSC reversing and non-reversing heat flow curves for the heating cycle of as-received Neo Sentalloy orthodontic archwire segments (Brantley et al., 2003).

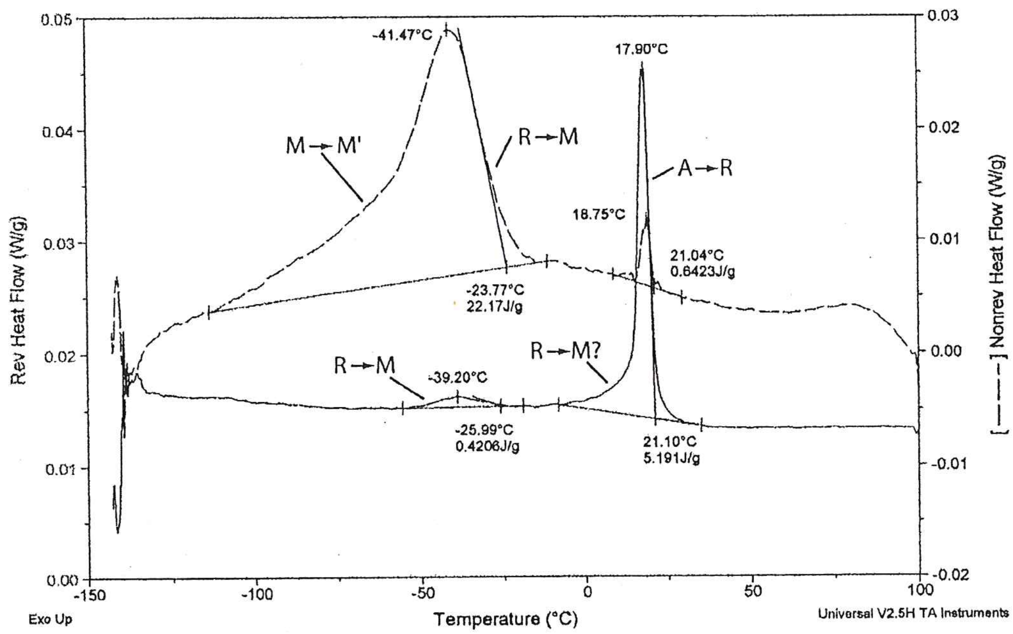

Figure 1.6: TMDSC reversing and nonreversing heat flow curves for the cooling cycle of as-received Neo Sentalloy orthodontic archwire segments (Brantley et al., 2003).

CHAPTER 2

SIGNIFICANCE AND HYPOTHESES

2.1 Significance

This study was designed to provide fundamental dental materials science information about the phase transformations in nickel-titanium rotary endodontic instruments. Such information may be pivotal for the future development of a new generation of improved instruments with reduced likelihood of failure during clinical use, which is presently of considerable concern with these instruments. The ultimate objective of this research area is to provide potential means for improving the clinical performance of NiTi rotary instruments, which will require future studies to assess.

2.2 Hypotheses

The *first* hypothesis for the present research was that microstructural phases and phase transformations have major impact on the clinical performance and failure process for these instruments. The *second* hypothesis was that appropriate heat treatments used for nickel-titanium orthodontic wires will result in significant changes in the microstructural phases in these instruments. The present research was designed to test these two hypotheses. It is expected that changes in NiTi microstructural phases resulting from appropriate heat treatment of the rotary endodontic instruments will be accompanied by beneficial changes in mechanical properties. Such changes, which will need to be extensively investigated in future research, should significantly affect the clinical life of these instruments.

CHAPTER 3

MICRO-X-RAY DIFFRACTION INVESTIGATION OF CLINICALLY USED NICKEL-TITANIUM ROTARY ENDODONTIC INSTRUMENTS

3.1. Introduction

There is conflicting evidence about the radial land design for nickel-titanium (NiTi) rotary endodontic instruments. Radial lands are the flat portions of the flutes between the edges (where rollover typically exists) on some instrument brands. The main purpose of radial lands is to keep the files centered in the canals. Ankrum et al. (2004) suggest that instruments with radial lands, such as ProFile (Dentsply Tulsa Dental) and K3 (SybronEndo) are more prone to permanent deformation but have lower incidence of fracture, compared to instruments without radial lands (ProTaper, Dentsply Tulsa Dental), as there is more friction between the radial land and the root dentin.

As discussed in Chapter 1, superelastic NiTi alloys take advantage of a stress-induced martensitic transformation to achieve high elastic strain (typically less than about 10%) without fracture. In a recent study we have shown that the NiTi rotary endodontic instruments fail in a complex manner consisting of both brittle and ductile aspects (Alapati et al., 2005). The presence of surface cracks created during machining of the instruments from the starting NiTi wire stock seems to be a major drawback, as dentin chips and other debris created during clinical instrumentation of the root canal can become lodged in these cracks, which can then propagate under the localized stress conditions and result in instrument fracture (Alapati et al., 2004).

Micro-X-ray diffraction (Micro-XRD) has been previously utilized by Iijima and his associates (Iijima et al., 2002a and 2002b) to investigate the phases present in very small analysis regions (less than 0.5 mm dimensions) of NiTi orthodontic wires. Micro-XRD can be used to determine the phases at various positions along the length of a rotary NiTi endodontic instrument, and this is not possible with conventional XRD because the dimensions of the analysis region are much larger compared to Micro-XRD.

Previous DSC studies of rotary NiTi endodontic instruments after simulated clinical use suggest that these instruments principally still have the austenite structure found in as-received (unused) instruments (Brantley et al., 2002a and 2002b). This is necessary for superelastic behavior. The purpose of this study was to use Micro-XRD to determine the microstructural phases in two different brands of rotary NiTi instruments after clinical use, for comparison to the results obtained by DSC.

3.2 Materials and Methods

Representative rotary nickel-titanium instruments with an unknown history of clinical use were obtained from the graduate Endodontic Clinics at the College of Dentistry: (a) ProFile GT with tapers ranging from .04 - .08 and tip size of 20 ISO [International Organization for Standardization] (Dentsply Tulsa Dental); (b) ProTaper S2, F1, and F2 (Dentsply Tulsa Dental), and K3 (Sybron Dental Specialties), with taper.04 and .06, tip 25 and length 25 mm; and (c) Quantec with .06 taper, tip 25 and length 25 mm (Analytic/Sybron Dental Specialties). Micro-XRD analyses (Rint-2000, Rigaku) were performed at room temperature using CuKα radiation at 40 kV and 300 mA. Analyses were performed on areas of approximately 50 μm diameter at the tip, and on the flattened flute surfaces (radial lands) at distances of 3 mm, 6 mm, 9 mm and 12 mm from the tip (D3, D6, D9 and D12).

3.3 Results and Discussion

For reference to the Micro-XRD results obtained in this study, a typical conventional x-ray diffraction pattern for a nickel-titanium orthodontic wire (40°C Copper Ni-Ti, Ormco) that contains both the austenite and martensite peaks is shown in Figure 3.1 (Brantley, 2001). The composition of this wire has been adjusted by the manufacturer to have an austenite-finish (A_f) temperature of approximately 40°C, at which the martensite is completely transformed to austenite. The peaks in Figure 3.1 have been labeled to indicate austenite (A) or martensite (M) and the specific diffracting plane.

It was found in this study that the tip regions of all specimens, except the used (permanently deformed) ProFile GT and as-received ProTaper instruments, had lower intensity for the main austenitic NiTi peak which occurs at a diffraction angle (2θ) of about 42.5° for CuKα x-rays (Brantley, 2001). Some main austenitic NiTi peak positions, especially from the tip area for ProFile GT and ProTaper, were slightly on the high-angle side, which suggests that this area probably contains R–phase or martensitic NiTi.

Examples of these Micro-XRD observations are shown in Figures 3.2 – 3.4. The lower intensity at the tip of the main austenitic NiTi peak for the as-received ProFile GT specimen shown in Figure 3.2 suggests that, as would be expected, the instrument had experienced greater work hardening in this region during manufacturing. The same behavior for the main austenite peak was found for the as-received K3 instrument shown in Figure 3.3 and for the used ProTaper instrument in Figure 3.4. The Micro-XRD patterns in Figures 3.2 – 3.4 were smoothed slightly and the backgrounds were subtracted, using software (Origin Pro 7.5) available with the Micro-XRD equipment. More smoothing can be readily achieved with the aid of this software, and the intensities and positions of the XRD peaks can be determined to high accuracy.

At this time, no specific relationship has been found for the main austenitic NiTi peak intensity at each analyzed area between the as-received instruments and the clinically used instruments. The Micro-XRD results in Figures 3.2 and 3.3 suggest that there is substantial variation in work hardening at different positions from the instrument tip as a result of the manufacturing process. The similar trend for the variation in main austenite peak intensity after clinical use (Figure 3.4) would be anticipated because of the dominant role of the tip region, where the greatest localized stresses are generated. The present Micro-XRD results do not appear to be in agreement with the results from previous Vickers hardness measurements suggesting that greater work hardening occurs at the middle regions along the instruments rather than at the tip (Alapati et al., submitted).

3.4 Conclusions

Micro-XRD analyses agree with DSC analyses that as-received nickel-titanium rotary endodontic instruments are in the austenitic condition required for superelastic behavior. Clinically used instruments remain largely in the austenitic condition, in agreement with the previous DSC analyses discussed in Chapter 1. The Micro-XRD results suggest that the tip region undergoes greater work hardening during the manufacturing process and that the relative amount of work hardening varies with distance from the tip.

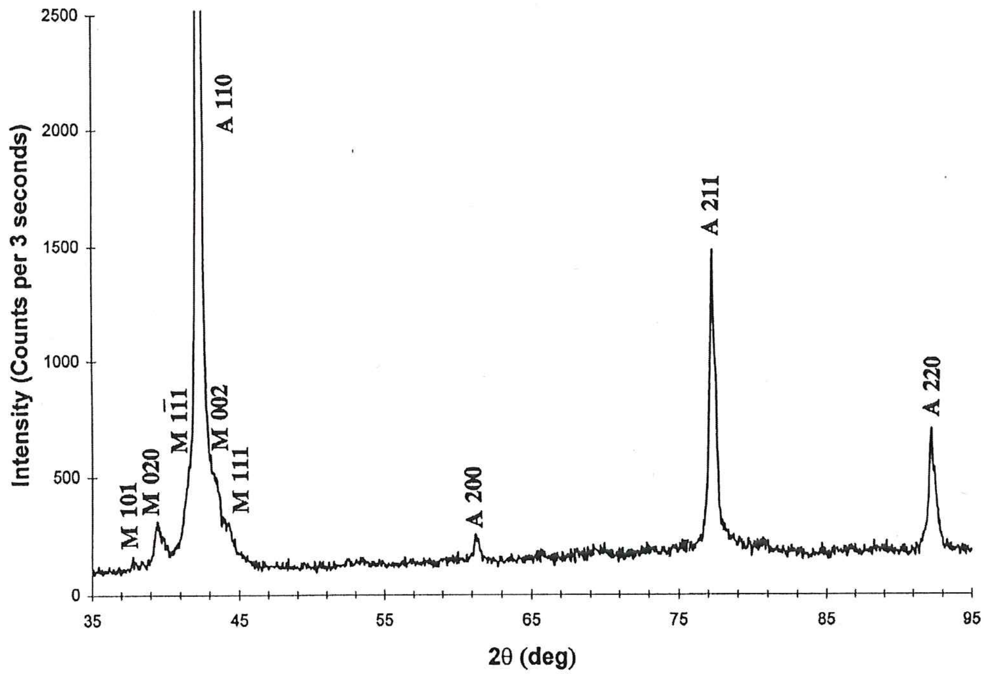

Figure 3.1: Conventional XRD pattern for 40°C Copper Ni-Ti with labeled austenite (A) and martensite (M) peaks (Brantley, 2001).

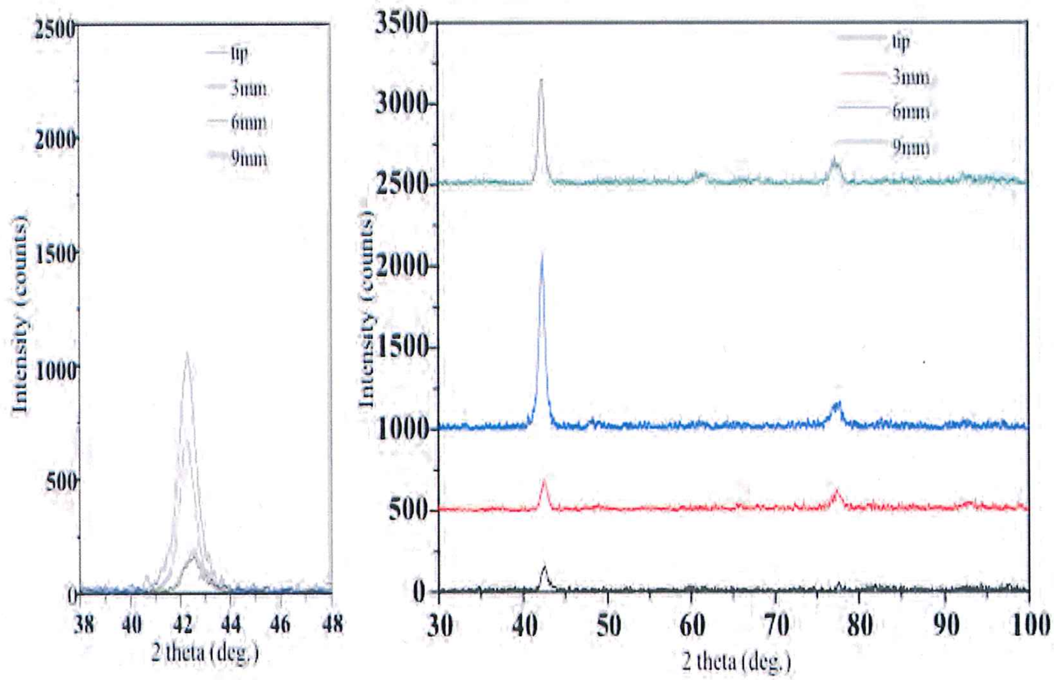

Figure 3.2: Micro-XRD patterns at various distances from the tip for an as-received ProFile GT/.06 taper NiTi rotary instrument. Only austenitic NiTi peaks are present. Peak identifications are shown in Figure 3.1.

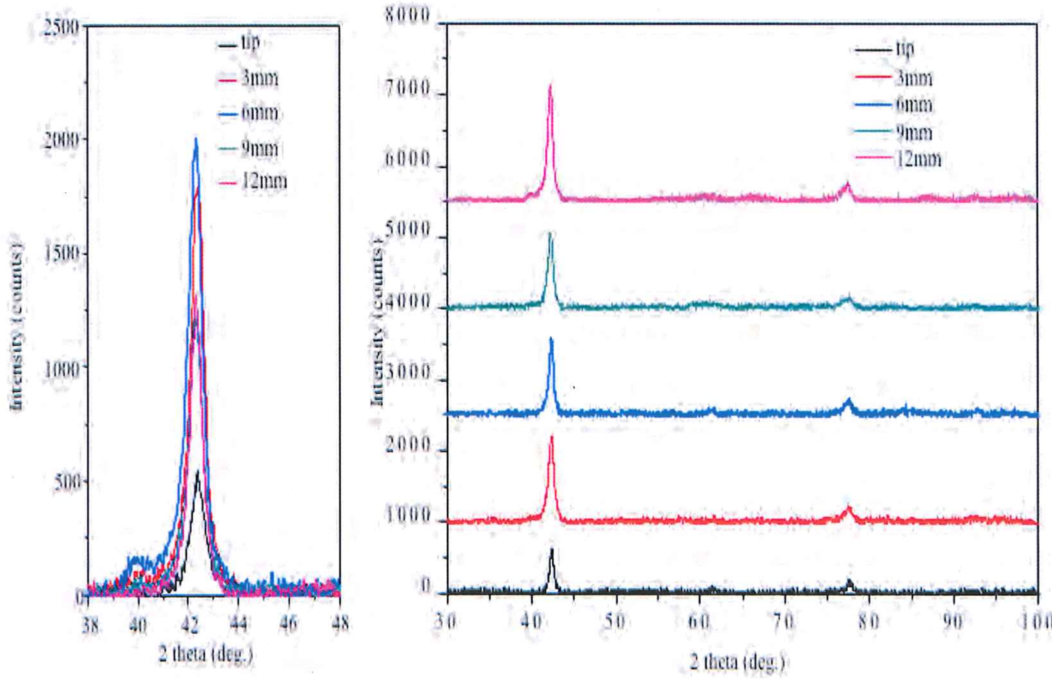

Figure 3.3: Micro-XRD patterns for an as-received K3 NiTi rotary instrument, showing the variation in intensity at various distances from the tip for the main austenite peak.

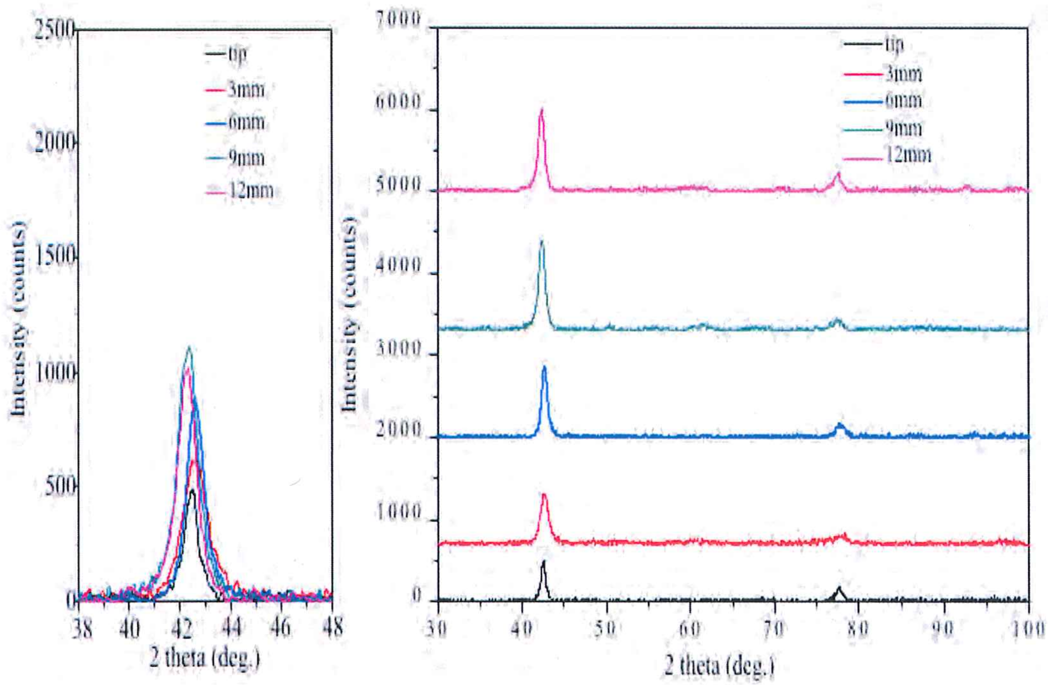

Figure 3.4: Micro-XRD patterns for a clinically used ProTaper NiTi rotary instrument, showing the variation in intensity for the main austenite peak at various distances from the tip.

CHAPTER 4

TEMPERATURE-MODULATED DSC INVESTIGATIONS OF PHASE TRANSFORMATIONS IN NEW AND CLINICALLY USED NICKEL-TITANIUM ROTARY ENDODONTIC INSTRUMENTS

4.1 Introduction

Endodontics is the dental specialization area that is concerned with the elimination of damaged, diseased or necrotic pulp tissue from the root canals of teeth, followed by the placement of appropriate filling and sealing materials. In current clinical endodontic practice, engine-driven rotary files placed in the dental handpiece are commonly used to rapidly enlarge the root canals to facilitate subsequent removal of pulp tissue (Blum et al., 2003; Hsu and Kim, 2004; Riitano, 2005). Rotary endodontic instruments fabricated from nickel-titanium are highly popular because the much lower elastic modulus of NiTi, compared to the austenitic stainless steel alloy from which traditional endodontic files and reamers have been fabricated, is highly advantageous for negotiating curved root canals (Walia et al., 1988).

The nickel-titanium alloy from which rotary endodontic instruments are fabricated is based upon the equiatomic NiTi phase in the nickel-titanium system

(Thompson, 2000). The NiTi alloy was first used in dentistry for orthodontics, and NiTi wires are available with three types of mechanical behavior in the oral environment: nonsuperelastic, superelastic (termed *pseudoelastic* in engineering materials science), and true shape-memory (Brantley, 2001). This mechanical behavior is determined by the relative proportions and characteristics of the three NiTi microstructural phases: martensite, austenite, and R–phase. Martensite is present at low temperatures and high stresses, while austenite is present at high temperatures and low stresses. The transformation from low-temperature martensitic NiTi to high-temperature austenitic NiTi on heating is completed at the austenite-finish (A_f) temperature. The R–phase can form as an intermediate phase during the forward transformation between martensite and austenite on heating and during the reverse phase transformation between austenite and martensite on cooling (Todoroki and Tamura, 1987). Differential scanning calorimetry (DSC) is commonly employed to study the phase transformation behavior in the nickel-titanium alloys for engineering (Todoroki and Tamura, 1987) and orthodontic (Yoneyama et al., 1992; Bradley et al., 1996) applications.

The manufacturing procedure for the nickel-titanium rotary endodontic instruments involves the machining of a wire blank into a variety of cross-sectional shapes that depend upon the particular product. Thompson (2000) states that these instruments are manufactured with the NiTi alloy in the superelastic condition, where the alloy has the austenitic structure. This statement is highly plausible, since extensive reversible elastic strain (up to approximately 10% for uniaxial tension) could then occur in the instrument when the stress in the root canal reaches a sufficiently high level that it causes transformation from austenite to martensite (Kuhn et al., 2001). Nonetheless, published verification of this superelastic condition was not obtained until recently from DSC experiments on representative nickel-titanium instruments in the as-received condition (Brantley et al., 2002a) and after simulated clinical use (Brantley et al., 2002b).

Recent temperature-modulated DSC (TMDSC) investigations of NiTi orthodontic wires (Brantley et al., 2002c and 2003) revealed that the transformations between martensite and austenite are more complicated than observed with conventional DSC, and appear to invariably involve the intermediate R–phase. The purpose of this study was to employ the greater resolution of TMDSC to investigate the phase transformations that occur in NiTi rotary endodontic instruments. Since these instruments are machined from NiTi wire blanks, it was anticipated that phase transformation processes similar to those occurring in the NiTi orthodontic wires would be encountered.

4.2 Materials and Methods

Two popular nickel-titanium rotary endodontic instruments which differ in cross-sectional designs (taper and flute designs) were selected for study: (a) ProFile GT, 25 mm in length, tip size 20 ISO with tapers .04, .06 and .08; (b) ProTaper, 25 mm in length, shapers (S2), finishers (F1 and F2) (both products from Dentsply Tulsa Dental). These instruments were analyzed using TMDSC in both the as-received condition and after clinical use (unknown history). For the latter, clinically discarded instruments were collected from the graduate Endodontic Clinic and grouped into three categories: (1) instruments with no visible deformation, (2) instruments with visible permanent deformation, and (3) instruments that had fractured during clinical use. Three randomly selected specimens were analyzed for each group for each of the two NiTi rotary instrument products.

Test specimens consisted of two to four segments, approximately 4 – 5 mm in length, that were carefully cut from the instruments, using a slow-speed water-cooled diamond saw. TMDSC studies (Q100, DSC, TA Instruments, Wilmington, DE) were performed over the temperature range from approximately –80° to 100°C, using a linear heating and cooling rate of 2°C per minute, with a superimposed sinusoidal oscillation having an amplitude of 0.318°C and a period of 60 seconds to provide heating-only conditions. The DSC cell was purged with nitrogen gas during the analyses, and deionized water and indium were used for temperature calibration. TMDSC plots were obtained for both the heating and cooling cycles, since the phase transformation behavior for the nickel-titanium alloy differs appreciably in the forward (heating) and reverse (cooling) directions. Since the use of a crimped pan top for better heat transfer might impose sufficiently high stress on the nickel-titanium alloy segments to alter the proportions of the NiTi phases, the test segments for each specimen were placed in an open pan; an empty aluminum pan served as the inert control specimen for the TMDSC analyses.

4.3 Results and Discussion

Figure 4.1 presents TMDSC plots for three representative test specimens obtained from as-received ProFile GT and ProTaper instruments. For each test specimen, the lower plot is for the initial heating cycle, and the upper plot is for the subsequent cooling cycle.

Only the total heat flow is shown in Figure 4.1 (and in Figures 4.2 and 4.3), similar to the graphical presentation for conventional DSC; the total heat flow has not been subdivided into the reversible and nonreversible components (Brantley et al. 2002c and 2003). The broad endothermic peak during the heating cycle on each plot is assumed to correspond to initial transformation from martensitic NiTi to R–phase, followed by the transformation at higher temperature from R–phase to austenitic NiTi. For the NiTi alloys in these rotary endodontic instruments, TMDSC is unable to resolve this broad peak into the two separate peaks for these heating transformations, although this has been done for NiTi orthodontic wires (Brantley et al., 2002c and 2003). Analogously, the broad exothermic peaks on the cooling curves are expected to correspond to the initial transformation from austenite to R–phase, followed by the subsequent transformation from R–phase to martensite, which also cannot be resolved by TMDSC although this is possible for orthodontic wires (Brantley et al., 2002c and 2003). It can be seen in Figure 4.1 that the phase transformation processes and overall enthalpy changes (ΔH) obtained from the areas under the peaks are similar for both products, which are in the superelastic (completely austenitic) condition at the temperature of the oral environment (37°C).

The TMDSC heating and cooling curves presented in Figure 4.2 compare test specimens obtained from a ProFile GT instrument that fractured during clinical use with an as-received instrument and an instrument that was permanently deformed without fracture during clinical use. The phase transformation behavior is similar for the three instrument conditions, with the as-received instrument having lower A_f temperature for the heating cycle, compared to the very similar A_f temperatures for the deformed and fractured instruments. Many more test specimens from as-received and clinically used instruments would need to be analyzed by TMDSC to verify that this result generally occurs, since there can be substantial differences in transformation behavior for as-received NiTi rotary instruments of the same product (Brantley et al., 2002a). Both the deformed without fracture and the fractured ProFile GT instruments retained superelastic behavior since their austenite-finish (A_f) temperatures were below 30°C. Figure 4.3 compares test specimens from clinically fractured ProFile GT and ProTaper instruments, which have phase transformation behavior very similar to that in Figures 4.1 and 4.2.

Figures 4.4 and 4.5 show the separate reversing and nonreversing heat flow curves, as well as the total heat flow curve, that were obtained by TMDSC for as-received ProFile GT and ProTaper instruments, respectively. Addition of the reversing and nonreversing heat flow curves yields the total heat flow curve for TMDSC, which was previously shown in Figures 4.1, 4.2 and 4.3. This relationship between the total, reversing and nonreversing heat flow curves is evident when Figures 4.4 and 4.5 are examined. It can be seen from comparison with Figures 4.1, 4.2 and 4.3 that little additional information was obtained for the phase changes in the NiTi rotary endodontic instruments from evaluation of the individual reversing and nonreversing heat flow curves. In particular well-defined separate peaks associated with transformations involving the R–phase were not found. This is in contrast to previous observations for shape memory and superelastic NiTi orthodontic wires (Brantley et al., 2002c and 2003), and is attributed to the substantial permanent deformation associated with the machining of these instruments from the starting wire blanks. Figures 4.4 and 4.5 show that both the forward and reverse transformations have substantial nonreversing character.

Table 4.1 summarizes the DSC results for all the as-received ProFile GT and ProTaper test specimens. This table presents (1) the range of ΔH values for the overall forward transformation from martensitic NiTi to austenitic NiTi on heating, (2) the range of ΔH values for the overall reverse transformation from austenitic NiTi to martensitic NiTi on cooling, and (3) the approximate A_f temperature at which the transformation to austenitic NiTi during heating was completed. As has been noted, the nickel-titanium alloys for both the ProFile GT and ProTaper instruments are in the expected (Thompson, 2000; Brantley et al., 2002a and 2002b) superelastic condition under clinical conditions, since transformation to the austenitic NiTi structure is completed by 25°C.

The ΔH values in Table 4.1 for the as-received ProFile GT and ProTaper rotary endodontic instruments, in Table 4.2 for the clinically fractured instruments of both types, and in Table 4.3 for the instruments of both types that permanently deformed during clinical use without fracturing lie within the range of 1.7 to 12.2 J/g (0.4 to 4.6 cal/g) reported for several nickel-titanium orthodontic wires (Brantley, 2001; Brantley et al., 2003). It can be seen in Tables 4.1 – 4.3 that the ΔH values for the overall forward and reverse transformations between martensitic NiTi and austenitic NiTi for each product were generally different. This can be due to manufacturing conditions of each type of instrument. However, similar results for a given transformation were obtained for the three conditions (as-received, fractured during clinical use, and permanently deformed without fracture during clinical use) of each product.

From the DSC results for shape memory orthodontic wires (Bradley et al., 1996; Brantley et al. 2002c and 2003), these nickel-titanium rotary instruments might possess shape memory at room temperature (and in the oral environment) if manufacturers used the proper processing steps. Future experimental measurements of the loading and unloading behavior of these instruments are necessary to establish the existence of shape memory and whether having this property would be of clinical relevance for endodontics, since the superelastic behavior possessed by the rotary instruments should be sufficient for negotiating curved canals without fracture.

4.4 Conclusions

These TMDSC studies show that the NiTi alloys for the clinically used ProTaper and ProFile GT instruments have only slightly different transformation temperatures and enthalpy changes for the overall transformation between martensite and austenite. Transformations involving the intermediate R–phase were not resolved by TMDSC, in contrast to previous studies on shape memory and superelastic NiTi orthodontic wire alloys. For each product, only small differences in transformation temperatures and enthalpy changes were observed for instruments in the as-received condition, instruments that were permanently deformed during clinical use, and clinically fractured instruments. These minor differences, which are perhaps insignificant, show that there are only small effects on the general phase transformation processes in the NiTi rotary instruments from variations in manufacturing processes associated with the instrument designs and from variations in the stresses to which the instruments are subjected during clinical use.

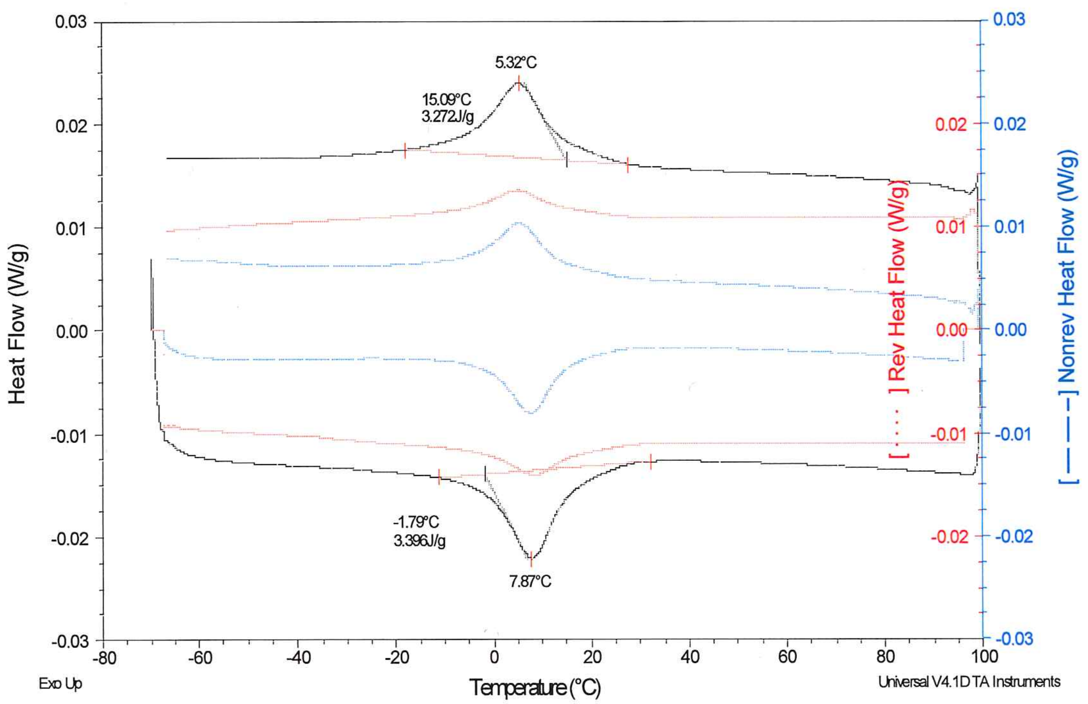

Figure 4.1: TMDSC curves for the heating (lower curves) and cooling cycles (upper curves) of test specimens obtained from a ProTaper rotary instrument in the as-received condition. The reversing and nonreversing, as well as the total, heat flow curves are shown for both the heating and cooling cycles. For the small scale at which the TMDSC results plotted by the computer software are shown, the dotted red line for the reversing heat flow curve appears as a continuous red line in this figure and in Figures 4.4 and 4.5. The use of construction lines to obtain enthalpy changes (ΔH) for transformations is illustrated. (The same style for presenting the heating and cooling curves is used in the other figures to follow.)

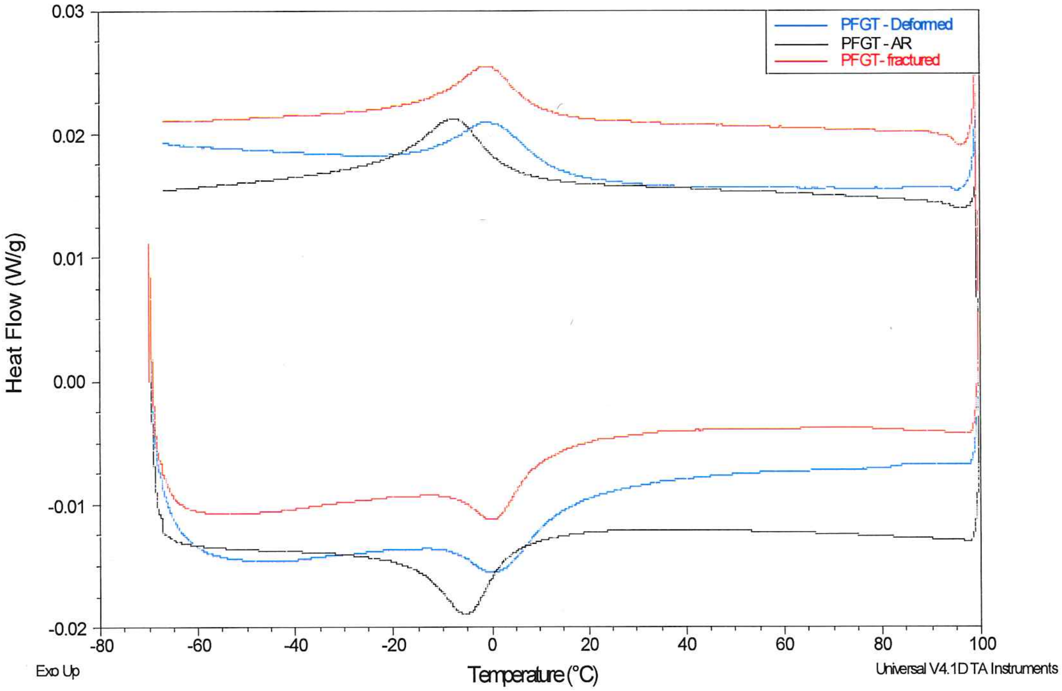

Figure 4.2: TMDSC curves (total heat flow) for test specimens consisting of segments from three ProFile GT instruments, comparing an instrument that was fractured during clinical use with an instrument that was permanently deformed during clinical use and an instrument in the as-received condition (AR).

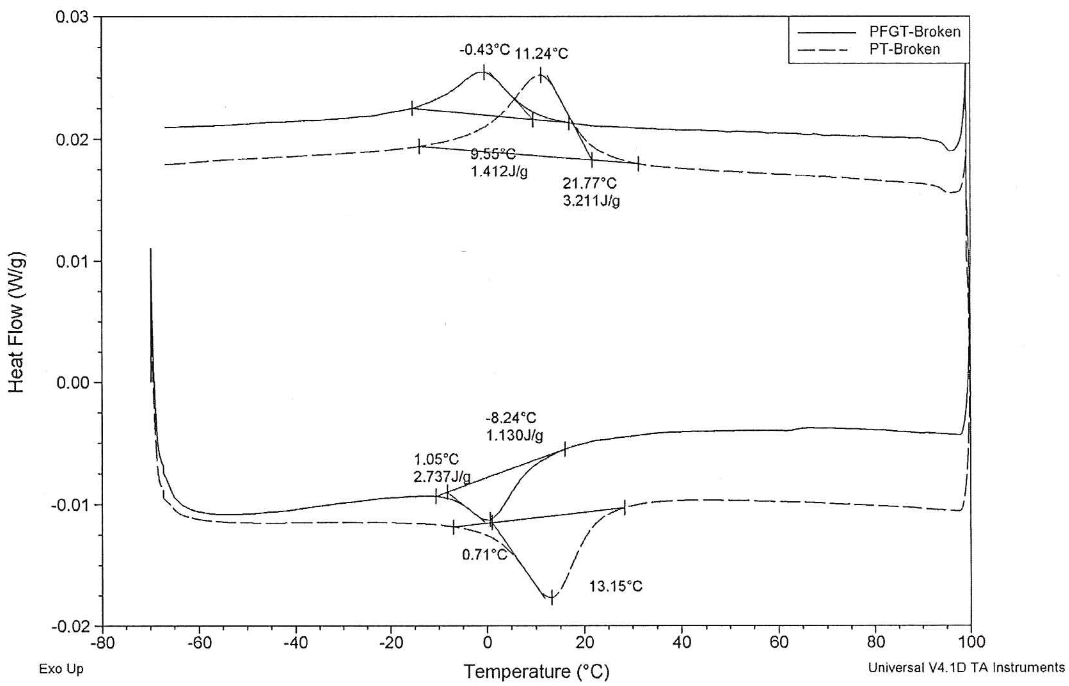

Figure 4.3: TMDSC curves (total heat flow) for test specimens consisting of segments obtained from ProFile GT (PFGT) and ProTaper (PT) instruments that fractured during clinical use.

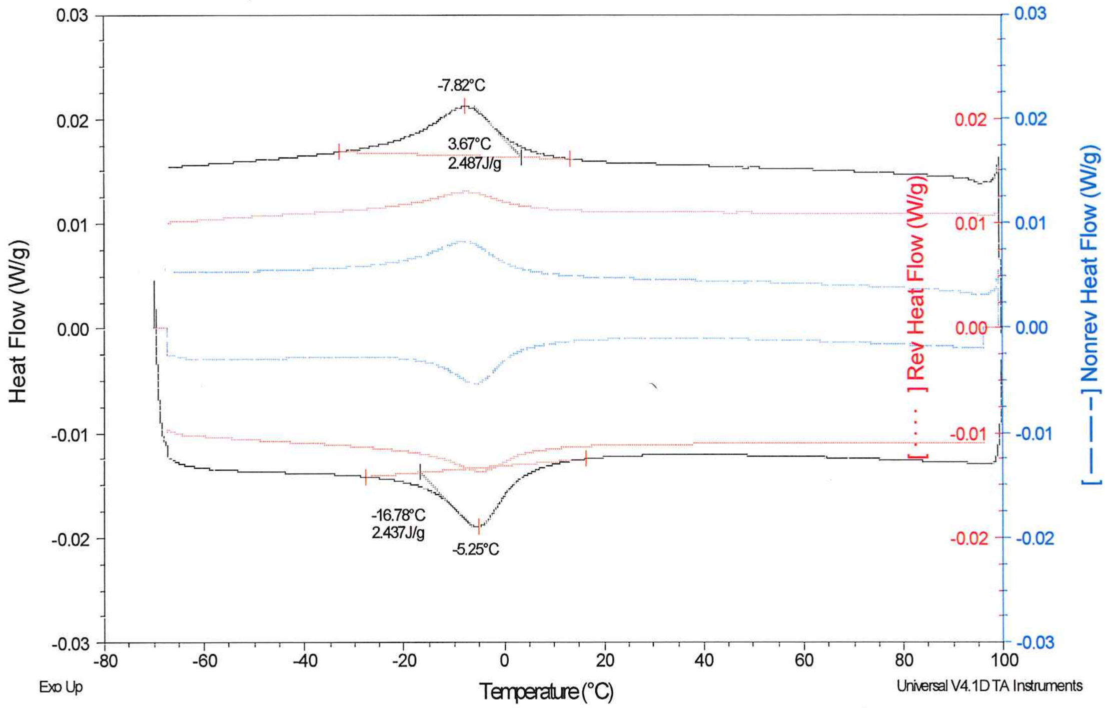

Figure 4.4: TMDSC curves for a test specimen obtained from an as-received ProFile GT rotary instrument. The reversing and nonreversing, as well as the total, heat flow curves are shown for both the heating and cooling cycles. The use of construction lines to obtain enthalpy changes (ΔH) for transformations is illustrated.

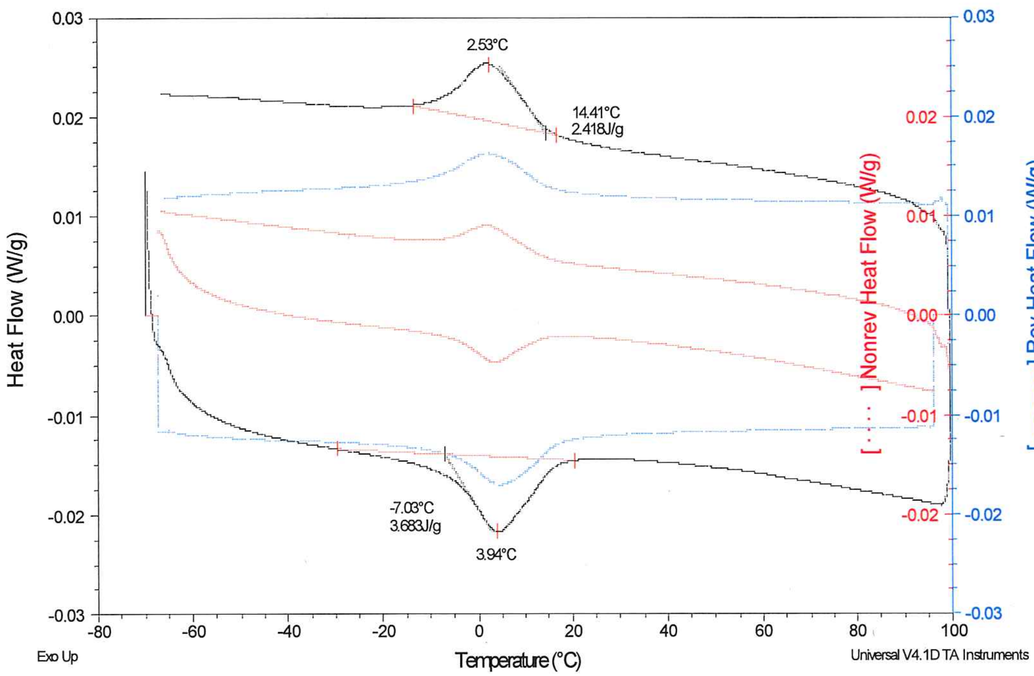

Figure 4.5: TMDSC curves showing total heat flow, reversing heat flow and nonreversing heat flow for the heating and cooling cycles of a test specimen consisting of several segments from an as-received ProTaper rotary instrument.

Property	ProFile GT	ProTaper
ΔH (martensitic NiTi to austenitic NiTi) on heating, J/g	1.9 to 2.3	1.8 to 2.9
ΔH (austenitic NiTi to martensitic NiTi) on cooling, J/g	1.4 to 2.5	1.5 to 2.2
Approximate completion temperature (A_f) for transformation to austenitic NiTi, °C	+21	+17

Table 4.1 Properties determined from the total heat flow curves on the TMDSC plots for the as-received ProFile GT and ProTaper rotary endodontic instruments.

Property	ProFile GT	ProTaper
ΔH (martensitic NiTi to austenitic NiTi) on heating, J/g	2.6 to 3.9	2.4 to 3.2
ΔH (austenitic NiTi to martensitic NiTi) on cooling, J/g	1.8 to 2.6	1.3 to 2.1
Approximate completion temperature (A_f) for transformation to austenitic NiTi, °C	+21	+19

Table 4.2 Properties determined from the TMDSC plots for the two types of rotary endodontic instruments that fractured during clinical use.

Property	ProFile GT	ProTaper
ΔH (martensitic NiTi to austenitic NiTi) on heating, J/g	2.1 to 3.9	1.8 to 2.4
ΔH (austenitic NiTi to martensitic NiTi) on cooling, J/g	2.8 to 3.6	1.8 to 2.6
Approximate completion temperature (A_f) for transformation to austenitic NiTi, °C	+22	+20

Table 4.3 Properties determined from the TMDSC plots for ProFile GT and ProTaper instruments that permanently deformed without fracturing during clinical usage.

CHAPTER 5

EFFECT OF HEAT-TREATMENT ON PHASE TRANSFORMATIONS IN NICKEL-TITANIUM ROTARY ENDODONTIC INSTRUMENTS

5.1 Introduction

One important aspect of root canal preparation is to preserve the natural curvature of the root canal system. This can be achieved by proper cleaning and shaping techniques. Nickel-titanium endodontic NiTi hand files were first introduced in the revolutionary work by Walia et al. (1988). Due to the very low elastic modulus for NiTi, these instruments are able to bend around the curvature of root canals without causing any major permanent damage. Alteration of the root canal shape/curvature during endodontic instrumentation is dependent on techniques and the instruments used by the operator (Riitano, 2005). Recent DSC experiments by Brantley et al. (2002a) have shown that the manufactured NiTi rotary instruments are in the superelastic condition under clinical conditions and may have shape memory characteristics (return to the original straight condition after removal from the canal). While preparing curved canals, these instruments tend to remove more dentin from the outer curvature of the dentinal wall

(Poulsen et al., 1995; Short et al., 1997 and 2001; Szep et al., 2001). Such preparations have a propensity to weaken the tooth structure, if over extended.

Rotary endodontic instruments fabricated from nickel-titanium alloys based upon the equiatomic intermetallic compound NiTi may exhibit reversible transformation from the parent austenitic structure (A) to the martensitic structure (M) under stresses that arise during preparation of curved root canals. Such transformations might have fundamental consequences for clinical performance of these instruments.

Phase transition temperatures of NiTi rotary endodontic instruments depend on important parameters such as chemical composition (Ni-Ti ratio), heat treatment and cold working. Several methods have been reported for studying phase transformations in orthodontic NiTi alloys, of which differential scanning calorimetry (DSC) (Yoneyama et al., 1992; Bradley et al., 1996) and measurements of electrical resistivity (Chen et al., 1992) are often utilized. DSC is highly convenient and provides direct information about temperatures for phase transformations as well as values of enthalpy changes that cannot be obtained by measurements of electrical resistivity. The latter also provides a highly convenient method for determining temperatures for phase-transformations and is readily employed at very low temperatures (Chen et al., 1992).

The primary objective of this study was to determine some heat treatment method to condition NiTi rotary instruments that might enhance clinical performance. The approach used to achieve this objective was to determine an apparent optimal heat treatment temperature for modifying the austenite phase transformation temperature. Heat treatment is one of the most fundamental approaches to adjust the transition temperature in NiTi alloys. Experimental procedures for performing the temperature-modulated DSC used in this investigation, and for interpreting the heating and cooling curves, were described in the preceding chapter.

5.2 Materials and Methods

ProFile GT instruments with .04, .06 and .08 tapers, and ISO tip size 20 (Dentsply Tulsa Dental) and ProTaper (Dentsply Tulsa Dental) instruments in F1, F2 and F3 sizes (both 25 mm in length) were selected, along with Liberator (Miltex) instruments in sizes 45 – 80 with .02 taper and 21 mm length. All three groups of instruments were subjected to 90° bending using a vise to hold the apical 3 mm, heat-treated for 15 minutes in a nitrogen atmosphere at 400°, 500° and 600°C, and then oven-cooled. The heat-treatment temperatures and time were based upon the Miura et al. (1986) study that introduced superelastic NiTi orthodontic wires. Some instruments were also heat-treated in the same manner at 850°C for 15 minutes to assess the effects of this higher heat-treatment temperature.

As-received, bent, and heat-treated instruments were cut into test specimens consisting of 3 or 4 segments approximately 4 – 5 mm in length. TMDSC analyses (DSC Q100, TA Instruments) were conducted as described in Chapter 4 between –80° and 100°C, using a linear heating and cooling rate of 2°C per minute and an oscillation amplitude of 0.318°C with a period of 60 seconds. Nitrogen was used as the purge gas

5.3 Results

The bent instruments showed minimal change in transformation temperature range (TTR) and enthalpy change for the overall transformation between the austenite (A) and martensite (M) phases, compared to as-received instruments of the same product. As noted in the previous chapter, the presence of the intermediate R–phase was again minimally evident with as-received test specimens and also with bent test specimens. Because the lowest starting temperature with this TMDSC apparatus for the initial heating cycle was –80°C, the large low-temperature exothermic peak on the nonreversing heat flow curve that arise from transformations within martensite for NiTi orthodontic wires (Brantley et al., 2002c and 2003) could not be observed in its entirety.

Figure 5.1 shows results of 400°C heat treatment for an as-received ProFile GT test specimen in a nitrogen atmosphere for 15 minutes. Because of the nearly symmetric nature of the broad curves, it is not possible to state that the overall transformation from martensite to austenite on heating has been resolved into two successive transformations: martensite to R–phase, followed by R–phase to austenite. However, the nonsymmetric nature of the cooling curves, which have a low-temperature tail, indicates that the reverse transformation from austenite to martensite takes place in two stages involving the intermediate R–phase, although the two peaks (Brantley et al., 2002c and 2003) cannot be resolved. Previous research with NiTi orthodontic wires indicates that heat treatment at 400°C does not affect their superelastic character (Miura et al., 1986; Khier et al., 1991). However, after heat treatment at 400°C, the A_f temperature of the NiTi alloy for the

ProFile GT test instrument shown in Figure 5.1 is approximately 50°C, substantially higher than the temperature of the oral environment.

The martensite-start and martensite-finish transformation temperatures (M_s, M_f) and the reverse austenite-start and austenite-finish transformation temperatures (A_s, A_f) were determined by software associated with the TMDSC apparatus. In initial experiments, after three thermal cycling runs with the TMDSC apparatus, test specimens experienced minimal change in transformation temperatures. Subsequently, each specimen was tested and analyzed during a single TMDSC thermal cycle run only.

Figure 5.2 shows the result of 850°C heat treatment in nitrogen atmosphere for 15 minutes. Such high-temperature heat treatment completely alters the starting wire microstructure (private communication from Special Metals Corporation of New Hartford, NY), which is highly undesirable for the rotary endodontic instruments (Brantley, 2001). It is evident that the phase transformation behavior is now much more complex than that in Figure 5.1. The A_f temperature for this heat-treated NiTi test specimen is now approximately 25°C.

Figure 5.3 presents the TMDSC results for a ProTaper test specimen after heat treatment at 500°C. Two peaks (martensite to R–phase and R–phase to austenite) are observed on the heating curve, whereas only a single peak for the direct transformation from austenite to martensite is resolved on the cooling curve. The slightly nonsymmetric nature (with a small high-temperature tail) of the peaks on the cooling curves suggests that a two-step transformation involving R–phase also occurs on cooling (Brantley et al., 2002c and 2003). The A_f temperature of the NiTi alloy for the ProTaper specimen shown in Figure 5.3 was approximately 55°C after the 500°C heat treatment.

Figure 5.4 presents the TMDSC total heat flow, reversing heat flow, and nonreversing heat flow curves for a ProTaper instrument after heat treatment at 600°C. As for Figure 5.3, the two peaks on the heating curve correspond to transformation from martensite to R–phase, followed by transformation from R–phase to austenite. The two peaks on the cooling curve may correspond to transformation from austenite to R–phase followed by transformation from R–phase to martensite, or alternatively transformation from austenite to martensite, followed by low-temperature transformation within martensite (Brantley et al., 2002c and 2003). The A_f temperature for this test specimen is approximately 50°C.

Figure 5.5 presents TMDSC plots (total heat flow curves) showing a comparison of the effects of heat treatments at 400°, 500°, and 600°C on test specimens from ProFile GT. The considerable increase in A_f temperature and the change in the nature of phase transformations between martensite and austenite after heat treatment, compared to the as-received condition, are evident.

5.4 Discussion

Heat treatment of NiTi rotary instruments between 400° and 600°C increases the austenite-finish (A_f) transformation temperature from approximately 25°C for as-received instruments to 50°C, which results in the loss of shape memory in the oral environment

(Brantley, 2001). Previous research on NiTi orthodontic wires has shown that the martensite phase in shape memory products has lower hardness than the austenite phase (Brantley, 2001), while little change occurs in the elastic modulus (Miura et al., 1986). Beneficial results might be that such heat-treated instruments could be precurved by the endodontist and better contoured to the root canal curvature, perhaps decreasing the extent of straightening of a curved canal that would otherwise occur with present NiTi instruments. Heat treatment in a nitrogen atmosphere might also lead to a harder surface from the formation of nitrides (Rapisarda et al., 2000; Tripi et al., 2002), which is beneficial to cutting efficiency. This will require evaluation in future studies using surface analytical techniques, along with *in vitro* comparison of cutting performance for heat-treated and as-received NiTi rotary instruments. From the present research, heat treatment at 500°C in a nitrogen atmosphere might yield the optimum microstructure and mechanical properties, with improved resistance to deformation and fracture for NiTi rotary instruments, but these hypotheses must be confirmed with future research.

Planned extensive Micro-XRD study of heat-treated instruments should provide information on microstructural phases that will determine which one of the preceding alternative interpretations of the TMDSC peaks is correct. Further research is currently underway to determine if heat treatment before and after use has an impact on clinical durability of the NiTi rotary instruments. Perhaps heat treatment procedures above 400°C might eliminate the need for the sterilization cycle that is presently performed on these instruments.

5.5 Conclusions

Heat treatment of NiTi rotary endodontic instruments in a nitrogen atmosphere between temperatures of 450°C and 600°C can have considerable effect on the microstructural phases. Although the increased austenite-finish temperature results in the loss of any shape memory under clinical conditions, beneficial property changes for the NiTi alloys may include the potential capability of precurving the instruments before clinical use and the possibility that the altered mechanical properties might lead to improved resistance to failure.

5.6 Acknowledgments

We would like to express our appreciation to Gary Dodge in the Department of Materials Science and Engineering for his technical assistance with the heat-treatment process. We also thank Dentsply Tulsa Dental for providing test sample instruments and Subash Gupta from Special Metals Corporation of New Hartford, NY for providing consultation on DSC analysis and heat treatment of nickel-titanium alloys.

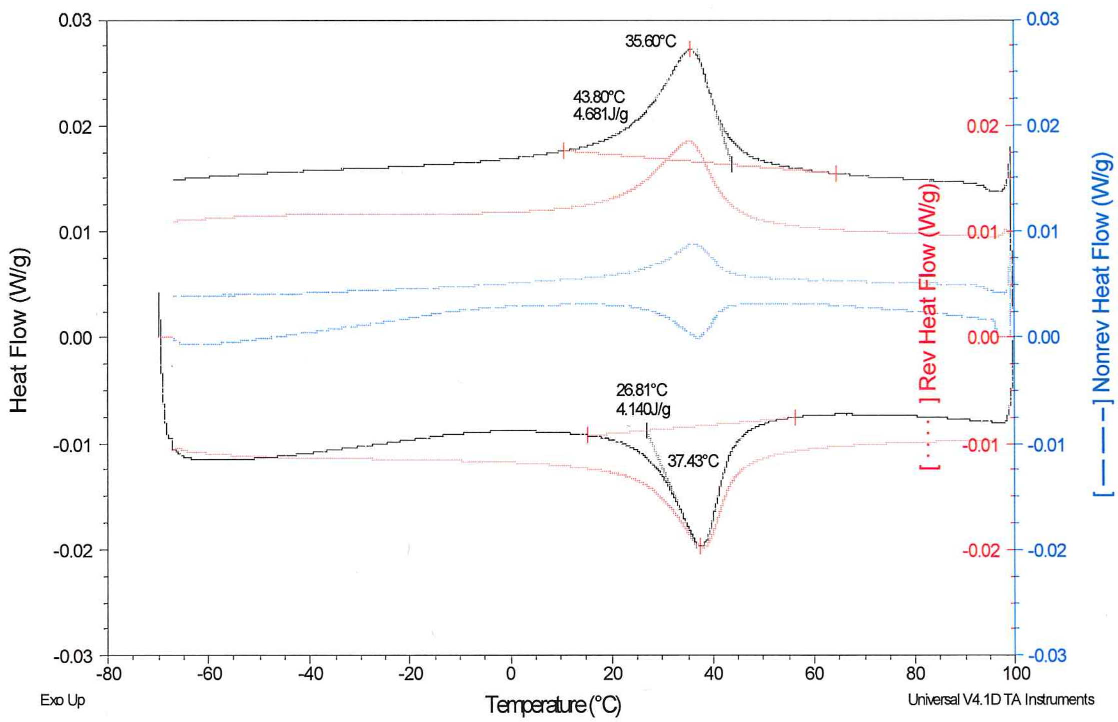

Figure 5.1: TMDSC total heat flow, reversing heat flow, and nonreversing heat flow curves for a ProFile GT test specimen after heating in a nitrogen atmosphere at 400°C for 15 minutes. As in Chapter 4, for the small scale at which the TMDSC results plotted by the computer software are shown, the dotted red line for the reversing heat flow curve appears as a continuous red line in Figures 5.1 through 5.4.

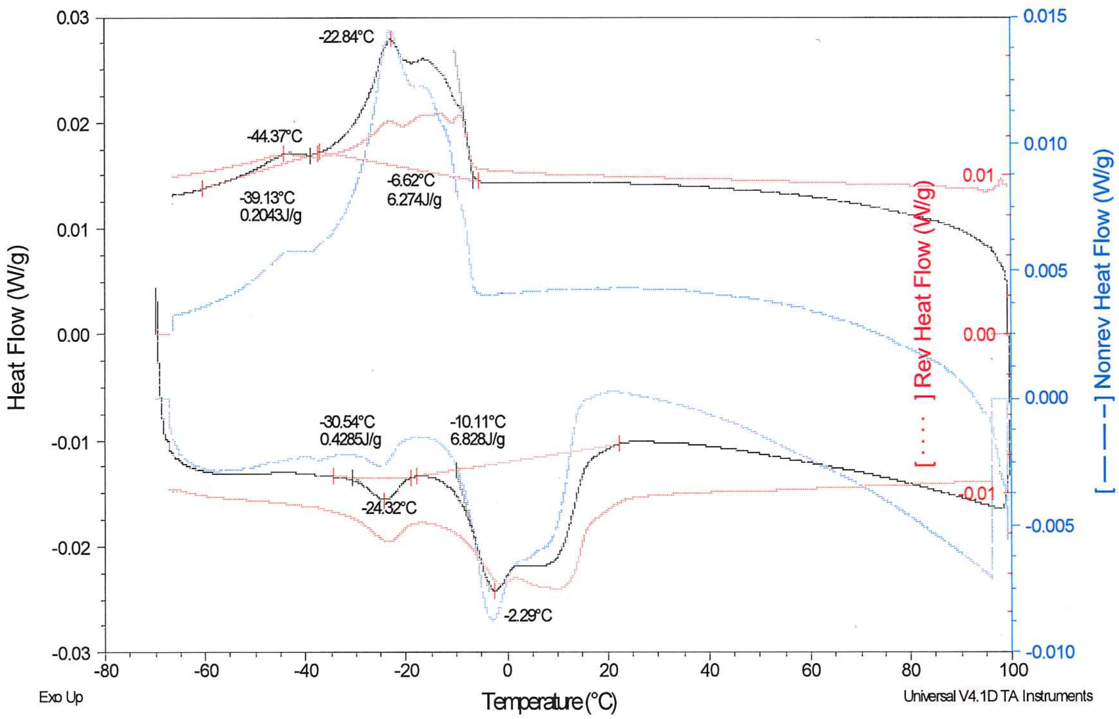

Figure 5.2: TMDSC total heat flow, reversing heat flow, and nonreversing heat flow curves for the heating and cooling cycles of a ProFile GT test specimen after heat treatment at 850°C in a nitrogen atmosphere for 15 minutes.

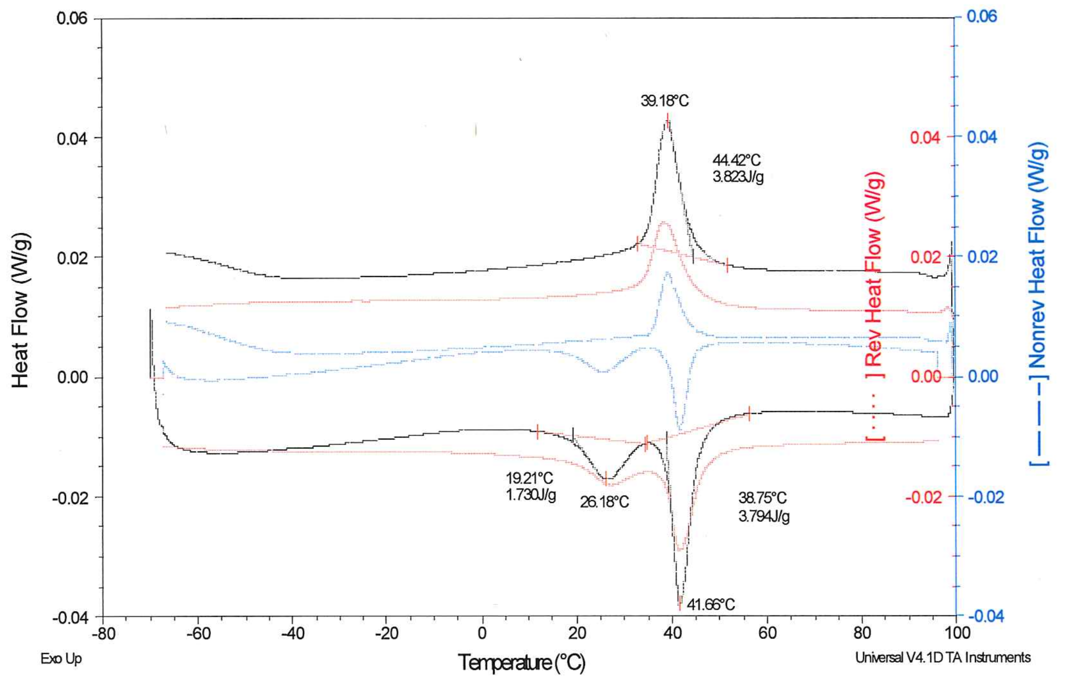

Fig 5.3: TMDSC total heat flow, reversing heat flow, and nonreversing heat flow curves for a ProTaper test specimen after heat treatment at 500°C for 15 minutes.

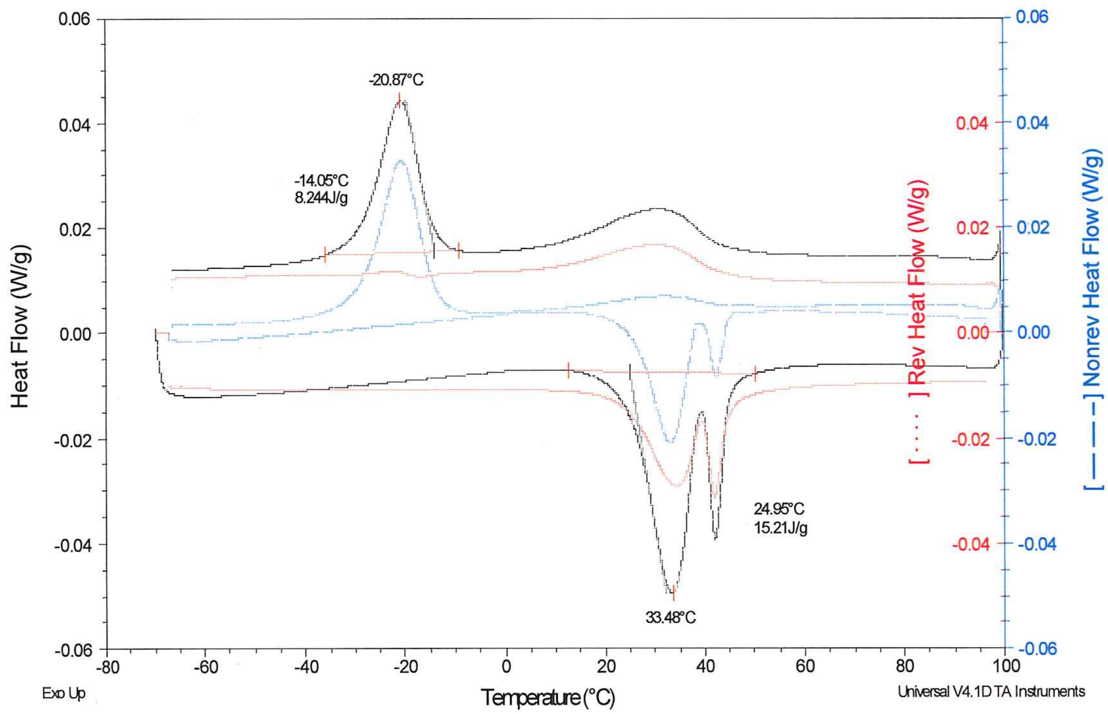

Fig 5.4: TMDSC total heat flow, reversing heat flow, and nonreversing heat flow curves for a ProTaper test specimen after heat treatment at 600°C for 15 minutes.

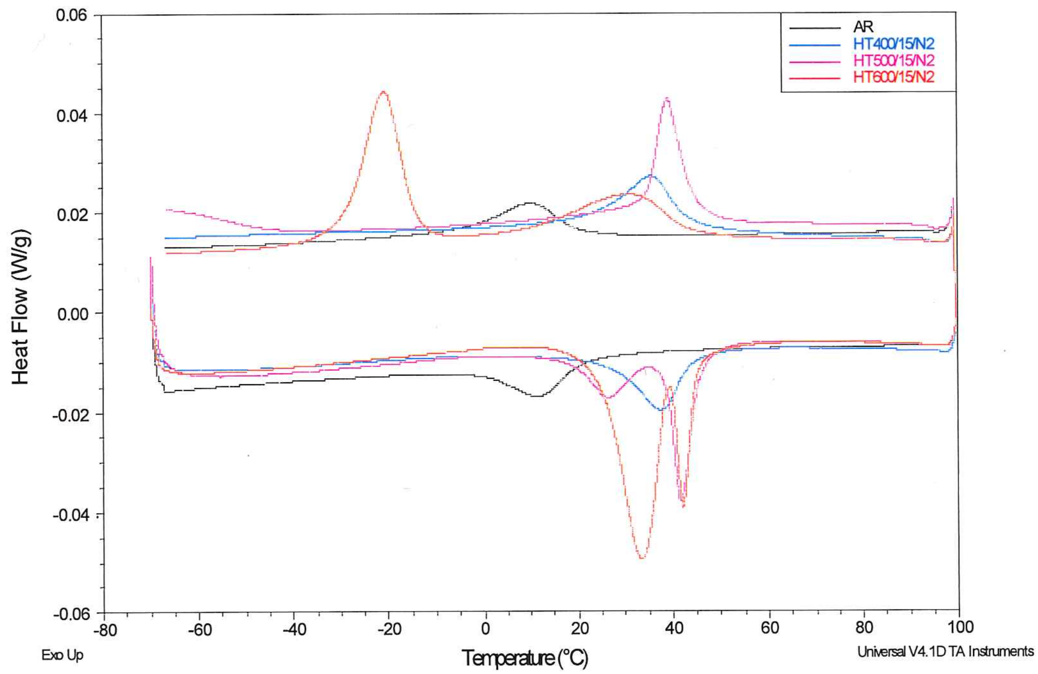

Fig 5.5: TMDSC plots (total heat flow) showing a comparison of the effects of heat treatments at 400°, 500°, and 600°C for 15 minutes on test specimens from ProFile GT.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Chapter 3. Micro-XRD investigation of clinically used nickel-titanium rotary endodontic instruments

The purpose of this study was to determine the phases at different distances from the tips of clinically use nickel-titanium rotary endodontic instrument, which is not possible with conventional x-ray diffraction because of the much larger analysis area. Under the conditions of this study, the following conclusions were drawn:

1. Micro-XRD analyses agree with DSC analyses that as-received nickel-titanium rotary endodontic instruments are in the austenitic condition required for superelastic behavior.
2. Clinically used instruments remain largely in the austenitic condition, in agreement with the previous studies that reported DSC analyses of similar instruments.
3. Micro-XRD results suggest that the tip region undergoes greater work hardening during the manufacturing process and that the relative amount of work hardening varies with distance from the tip.

Chapter 4. Temperature-modulated DSC investigations of phase transformations in new and clinically used nickel-titanium rotary endodontic instruments

The phase transformation process in nickel-titanium rotary instruments is complex at the atomic scale. These transformations are sensitive to instrument processing by the manufacturer and the Ni-Ti ratio in the alloy composition. Use of TMDSC provides much detailed information about the transformation process. Under the conditions of this study, the following conclusions were drawn:

1. ProTaper and ProFile have slightly different transformation temperatures and enthalpy changes. For a given product, the transformation temperatures and enthalpy changes are similar for the as-received instruments, instruments that are deformed without fracture during clinical use, and clinically failed instruments.
2. Small differences in transformation temperatures and enthalpy changes can be related to the manner in which different instruments deform under various stress conditions. This deformation can be related to the design of the instrument grooves. Previous research by this investigator has shown that instrument design and surface cracks from the manufacturing process have a key role for the tight lodging of dentin debris in the instrument surface, which becomes extremely hard to clean ultrasonically.

Chapter 5. Effect of heat-treatment on phase transformations in nickel-titanium rotary endodontic instruments

The primary objective of this investigation was to provide some heat treatment method to condition NiTi rotary instruments that might enhance clinical performance. The approach used to achieve this objective was to determine the effects of heat treatment temperature on modifying temperature at which the austenite phase transformation is completed. Heat treatment is one of the most fundamental approaches for adjusting the transition temperature in NiTi alloys. Suggestions are also offered about minimizing the clinical failure of the nickel-titanium instruments. Under the conditions of this study, the following conclusions were drawn:

1. Heat treatment of NiTi rotary endodontic instruments in a nitrogen atmosphere between temperatures of 450°C and 600°C for 15 minutes can have a considerable effect on the microstructural phases.
2. Possible beneficial property changes for the NiTi alloys after such heat treatment include the potential capability of precurving the instruments before clinical use and the possibility that the altered mechanical properties might lead to improved resistance to failure.

REFERENCES CITED

Alapati SB, Brantley WA, Svec TA, Powers JM, Mitchell JC (2003). Scanning electron microscope observations of new and used nickel-titanium rotary files. J Endod 29:667-9.

Alapati SB, Brantley WA, Svec TA, Powers JM, Nusstein JM, Daehn GS (2004). Proposed role of embedded dentin chips for the clinical failure of nickel-titanium rotary instruments. J Endod 30:339-41.

Alapati SB, Brantley WA, Svec TA, Powers JM, Nusstein JM, Daehn GS (2005). SEM observations of nickel-titanium rotary endodontic instruments that fractured during clinical use. J Endod 31:40-3.

Alapati SB, Brantley WA, Nusstein JM, Daehn GS, Svec TA, Powers JM, Johnston WM, Guo W. Vickers hardness investigation of work-hardening in used NiTi rotary instruments. J Endod (submitted).

Ankrum MT, Hartwell GR, Truitt JE (2004). K3 Endo, ProTaper, and ProFile systems: breakage and distortion in severely curved roots of molars. J Endod 30:234-7

Bahia MG, Martins RC, Gonzalez BM, Buono VT (2005). Physical and mechanical characterization and the influence of cyclic loading on the behaviour of nickel-titanium wires employed in the manufacture of rotary endodontic instruments. Int Endod J 38:795-81.

Berutti E, Chiandussi G, Gaviglio I, Ibba A (2003). Comparative analysis of torsional and bending stresses in two mathematical models of nickel-titanium rotary instruments: ProTaper versus ProFile. J Endod 29: 15-9.

Blum JY, Machtou P, Ruddle C, Micallef JP (2003). Analysis of mechanical preparations in extracted teeth using ProTaper rotary instruments: value of the safety quotient. J Endod 29:567-75.

Bradley TG, Brantley WA, Culbertson BM (1996). Differential scanning calorimetry (DSC) analyses of superelastic and nonsuperelastic nickel-titanium orthodontic wires. Am J Orthod Dentofac Orthop 110:553-8.

Brantley WA (2001). Orthodontic wires. In: Brantley WA, Eliades T, editors. Orthodontic Materials: Scientific and Clinical Aspects. Stuttgart: Thieme, pp. 77-103.

Brantley WA, Svec TA, Iijima M, Powers JM, Grentzer TH (2002a). Differential scanning calorimetric studies of nickel titanium rotary endodontic instruments. J Endod 28:567-72.

Brantley WA, Svec TA, Iijima M, Powers JM, Grentzer TM (2002b). Differential scanning calorimetric studies of nickel-titanium rotary endodontic instruments after simulated clinical use. J Endod 28:774-8.

Brantley WA, Iijima M, Grentzer TH (2002c). Temperature-modulated DSC study of phase transformations in nickel-titanium orthodontic wires. Thermochimica Acta 392-393:329-37.

Brantley WA, Iijima M, Grentzer TH (2003). Temperature-modulated DSC provides new insight about nickel-titanium wire transformations. Am J Orthod Dentofacial Orthop 124:387-94.

Chen R, Zhi YF, Arvystas MG. Advanced Chinese NiTi alloy wire and clinical observations. Angle Orthod 1992;62:59-66.

Cheung GS (1996). Endodontic failures—changing the approach. Int Dent J 41:131-8.

Civjan S, Huget EF, DeSimon LB (1975). Potential applications of certain nickel-titanium (nitinol) alloys. J Dent Res 54: 89-96.

Cohen S, Burns RC (2002). Pathways of the Pulp 8th edition, St. Louis: Mosby, pp 178-189.

Goldstein D, Kabacoff L, Tydings J (1987). Stress effects on nitinol phase transformations. J Metals 39:19-26.

Hsu YY, Kim S (2004). The ProFile system. Dent Clin North Am 48:69-85.

Iijima M, Ohno H, Kawashima I, Endo K, Mizoguchi I (2002a). Mechanical behavior at different temperatures and stresses for superelastic nickel-titanium orthodontic wires having different transformation temperatures. Dent Mater 18:88-93.

Iijima M, Ohno H, Kawashima I, Endo K, Brantley WA, Mizoguchi I (2002b). Micro X-ray diffraction study of superelastic nickel-titanium orthodontic wires at different temperatures and stresses. Biomaterials 23:1769-74.

Khier SE, Brantley WA, Fournelle RA (1991). Bending properties of superelastic and nonsuperelastic nickel-titanium orthodontic wires. Am J Orthod Dentofacial Orthop 99:310-8.

Kuhn G, Jordan L (2002) Fatigue and mechanical properties of nickel-titanium endodontic instruments. J Endod 2002 28:716-20.

Kuhn G, Tavernier B, Jordan L (2001). Influence of structure on nickel-titanium endodontic instruments failure. J Endod 2001;27:516-20.

Lee DH, Park B, Saxena A, Serene TP (1996). Enhanced surface hardness by boron implantation in Nitinol alloy. J Endod 22:543-6.

Manning SA (1990a). Root canal anatomy of mandibular second molars. Part I. Int Endod J 1990 23:34-9.

Manning SA (1990b). Root canal anatomy of mandibular second molars. Part II. C-shaped canals. Int Endod J 23:40-5.

Martins RC, Bahia MG, Buono VT (2002). Surface analysis of ProFile instruments by scanning electron microscopy and X-ray energy-dispersive spectroscopy: a preliminary study. Int Endod J 35: 848-53.

Miura F, Mogi M, Ohura Y, Hamanaka H (1986). The super-elastic property of the Japanese NiTi alloy wire for use in orthodontics. Am J Orthod Dentofacial Orthop 90:1-10.

Patino PV, Biedma BM, Liebana CR, Cantatore G, Bahillo JG (2005). The influence of a manual glide path on the separation rate of NiTi rotary instruments. J Endod 31:114-6.

Poulsen WB, Dove SB, del Rio CE (1995). Effect of nickel-titanium engine-driven instrument rotational speed on root canal morphology. J Endod 21:609-12.

Rangel S, Cremonese R, Bryant S, Dummer P (2005). Shaping ability of RaCe rotary nickel-titanium instruments in simulated root canals. J Endod 31:460-3.

Rapisarda E, Bonaccorso A, Tripi TR, Fragalk I, Condorelli GG (2000). The effect of surface treatments of nickel-titanium files on wear and cutting efficiency. Oral Surg Oral Med Oral Pathol Oral Radiol Endod 89:363-8.

Riitano F (2005). Anatomic Endodontic Technology (AET) — a crown-down root canal preparation technique: basic concepts, operative procedure and instruments. Int Endod J 38:575-87.

Sattapan B, Nervo GJ, Palamara JEA, Messer H (2000). Defects in rotary nickel-titanium files after clinical use. J Endod 26:161-5.

Short JA, Morgan LA, Baumgartner JC (1997). A comparison of canal centering ability of four instrumentation techniques. J Endod 23:503-7.

Sidow SJ, West LA, Liewehr FR, Loushine RJ (2000). Root canal morphology of human maxillary and mandibular third molars. J Endod 26 :675-8.

Szep S, Gerhardt T, Leitzbach C, Luder W, Heidemann D (2001). Preparation of severely curved simulated root canals using engine-driven rotary and conventional hand instruments. Clin Oral Investig 5:17-25.

Thayer TA, Bagby MD, Moore RN, DeAngelis (1995) RJ. X-ray diffraction of nitinol orthodontic arch wires. Am J Orthod Dentofacial Orthop 107:604-12.

Thompson SA (2000). An overview of nickel-titanium alloys used in dentistry. Int Endod J 33:297-310.

Todoroki T, Tamura H (1987). Effect of heat treatment after cold working on the phase transformation in TiNi alloys. Trans Japan Inst Metals 28:83-94.

Tripi TR, Bonaccorso A, Rapisarda E, Tripi V, Condorelli GG, Marino R, Fragala I (2002). Depositions of nitrogen on NiTi instruments. J Endod 28:497-500.

Tripi TR, Bonaccorso A, Tripi V, Condorelli GG, Rapisarda E (2001). Defects in GT rotary instruments after use: an SEM study. J Endod 27:782-5.

Walia H, Brantley WA, Gerstein H (1988). An initial investigation of the bending and torsional properties of nitinol root canal files. J Endod 14: 346-351.

Yoneyama T, Doi H, Hamanaka H, Okamoto Y, Mogi M, Miura F (1992). Super-elasticity and thermal behavior of NiTi alloy orthodontic arch wires. Dent Mat J 11: 1-10.

BIBLIOGRAPHY OF OTHER IMPORTANT ARTICLES

Abel E, Luo H, Pridham M, Slade A (2004). Issues concerning the measurement of transformation temperatures of NiTi alloys. Smart Materials and Structures 13:1110-17.

Andreasen G (1980). A clinical trial of alignment of teeth using a 0.019-inch thermal nitinol with a transition temperature range between 31°C and 45°C. Am J Orthod 88;528-37.

Andreasen GF, Bigelow H, Andrew JG (1979). 55 nitinol wire: Force developed as a function of "elastic memory". Aust Dent J 24:146-9

Andreasen GF, Morrow RE (1978). Laboratory and clinical analyses of nitinol wire. Am J Orthod 73:142-51.

Buehler WJ, Gilfrich JV, Wiley RC (1963) Effect of low-temperature phase changes on the mechanical properties of alloys near composition TiNi. J Appl Phys 34:1475.

Buehler WJ, Wang FE (1968). A Summary of recent research on the nitinol alloys and their potential applications in ocean engineering. Ocean Eng 105-20.

Calberson FL, Deroose CA, Hommez GM, Raes H, De Moor RJ. (2002) Shaping ability of GTTM rotary files in simulated resin root canals. Int Endod J 35:607-14.

Dieter GE (1986). Mechanical metallurgy, 3rd edition. New York: McGraw-Hill, 1986. pp. 254-6, 262-4, 394-8.

Eggert C, Peters O, Barbakow F (1999). Wear of nickel-titanium Lightspeed instruments evaluated by scanning electron microscopy. J Endod 25:494-7.

Fabra-Campos H, Rodriguez-Vallejo J (2001). Digitization, analysis and processing of dental images during root canal preparation with Quantec Series 2000 instruments. Int Endod J 34:29-39.

Gambarini G (2001). Cyclic fatigue of nickel-titanium rotary instruments after clinical use with low- and high-torque endodontic motors. J Endod 27:772-4.

Griffiths IT, Chassot AL, Nascimento MF, Bryant ST, Dummer PM (2001). Canal shapes produced sequentially during instrumentation with Quantec SC rotary nickel-titanium instruments: a study in simulated canals. Int Endod J 34:107-12.

Hata G, Uemura M, Kato AS, Imura N, Novo NF, Toda T (2002). A comparison of shaping ability using ProFile, GT file, and Flex-R endodontic instruments in simulated canals. J Endod 28:316-21.

Kuhn G, Tavernier B, Jordan L (2001). Influence of structure on nickel-titanium endodontic instruments failure. J Endod 27:516-20.

Li U-M, Lee BS, Shih CT, Lan WH, Lin CP (2002). Cyclic fatigue of endodontic nickel titanium rotary instruments: static and Dynamic tests. J Endod 28:448-51.

Melton KN (1990). Ni-Ti based shape memory alloys. In: Duerig TW, Melton KN, Stöckel D, Wayman CM, editors. Engineering aspects of shape memory alloys. Butterworth-Heinemann, London: 21-35.

Mize S, Clement D, Pruett J, Carnes D. (1998). Effect of sterilization on cyclic fatigue of rotary nickel-titanium endodontic instruments. J Endod 24:843-47.

Morison ME, Holcomb JB (1988). The MCV crown-down technique: a modified alternative coronal-flaring approach for endodontics. Va Dent J 65:32-8.

Peters OA, Kappeler S, Bucher W, Barbakow F (2002a). Engine-driven preparation of curved root canals: measuring cyclic fatigue and other physical parameters. Aust Endod J 28:11-7.

Ponti TM, McDonald NJ, Kuttler S, Strassler HE, Dumsha TC (2002). Canal-centering ability of two rotary file systems. J Endod 28:283-6.

Rapisarda E, Bonaccorso A, Tripi TR, Condorelli GG, Torrisi L (2001). Wear of nickel-titanium endodontic instruments evaluated by scanning electron microscopy: Effect of ion implantation. J Endod 27:588-92.

Schafer E, Florek H (2003). Efficiency of rotary nickel-titanium K3 instruments compared with stainless steel hand K-Flexofile. Part 1. Shaping ability in simulated curved canals. Int Endod J 36: 199-207.

Schafer E, Schlingemann R (2003). Efficiency of rotary nickel-titanium K3 instruments compared with stainless steel hand K-Flexofile. Part 2. Cleaning effectiveness and shaping ability in severely curved root canals of extracted teeth. Int Endod J 36:208-17.

Svec TA, Powers JM (2002). The deterioration of rotary nickel-titanium files under controlled conditions. J Endod 28:105-7.

Thompson SA, Dummer PM (1997a). Shaping ability of ProFile .04 Taper Series 29 rotary nickel-titanium instruments in simulated root canals. Part 1. Int Endod J 30:1-7.

Thompson SA, Dummer PM (1997b). Shaping ability of ProFile .04 Taper Series 29 rotary nickel-titanium instruments in simulated root canals. Part 2. Int Endod J 30:8-15.

Tygesen YA, Steiman HR, Ciavarro C (2001). Comparison of distortion and separation utilizing ProFile and Pow-R nickel-titanium rotary files. J Endod 27:762-4.

Wang FE, Pickart SJ, Alperin HA (1972). Mechanisms of the NiTi martensitic transformation and crystal structures of Ni-T II and NiTi III phases. J Appl Phys 43;97-112.

Wasilewski RJ (1971). The effects of applied stress on the martensitic transformation in TiNi. Met Trans 2:2973-81.

Yun HH, Kim SK (2003). A comparison of the shaping abilities of 4 nickel-titanium rotary instruments in simulated root canals. Oral Surg Oral Med Oral Pathol Oral Radiol Endod 95:228-33.