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Microstructural and mechanical characterizations of new Ni-Ti endodontic instruments

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Abstract. NiTi alloys have been used for many years in dentistry, especially in endodontology. High flexibility of NiTi alloys, compared to the stainless steel one, has made of NiTi the alloy of choice for the new generation of shaping files. Despite the improvement of file design, endodontic NiTi instruments are not perfect and the risk of fracture during use is still a concern. In recent years, several new thermomechanical processes have been developed to optimize the structure of NiTi alloys, in particular, the development of treatments named "M-wire", "R phase" and "CM wire" technologies. According to the manufacturers, these innovative treatments may improve the flexibility and the fatigue life of endodontic instruments. In the present work, new generations of these files have been characterized using DSC and bending tests and compared to a conventional NiTi file. The new endodontic instruments seem to improve the instrument properties. Hypotheses on the microstructural modifications due to specific thermomechanical treatments are proposed.

1 Introduction

NiTi alloys have been used for many years in dentistry, especially in endodontology [1]. The objectives of this treatment are the excision of the entire pulp tissue, whether inflamed or infected, and to obtain a clean and properly shaped canal, to insert a filling material [2]. The complexity of the root canal anatomy and the presence of curvatures found predominantly in the apical third of the root require the use of resistant and particularly flexible instruments. The arrival on the market in the 80s of nickel titanium instruments initiated a revolution in endodontic. The great flexibility of NiTi alloys gives the endodontic instrumentation undeniable qualities compared to that of stainless steels. It provides safer preparations, even in the canals with curvatures. However, the unexpected risk of fractures (torsional and flexural fractures) of the instrument is a major concern for clinicians.

Since 2007, the manufacturers propose new innovative manufacturing processes in order to improve the flexibility and the fatigue life of endodontic instruments [3]. Each firm named its proprietary thermomechanical process with a specific name like "M-wire", "R phase" and "Controlled Memory (CM) wire" technologies. From manufacturer descriptions, "M-wire" would be produced by applying "specific tensions and heat treatments at various temperatures" [4,5]; "R phase" instruments would be "twisted by a thermal process" during the R-Phase transformation [5,6] and "CM wire" would be a novel NiTi alloy using a special thermomechanical process that controls the memory of the material [5,7]. However, no more information on the real thermomechanical treatments is given.

From the literature, most NiTi files used in odontology are manufactured from commercially wires of Nitinol that contain approximately 55.8 wt.% nickel with titanium accounting for the balance. A series of cold work, followed by heat treatments are conducted. Two strategies can be followed for these heat treatments. On one hand, the alloy can be annealed directly at temperatures ranging between 350 and 450°C. On the other hand, the alloy is solution treated (between 600 and 900°C) and then aged around 400°C [8,9].

The aim of this study is to analyze the relationship between the microstructure (phases, transformations) and the mechanical behavior of these new generations of instruments. Hypotheses on the microstructural modifications due to the specific thermomechanical treatments will be proposed.

2 Materials and methods

2.1 Materials

Three new generation and one conventional NiTi endodontic instruments, dedicated to the preparation of

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the apical third (extremity) of the dental root, were analyzed. All types of files were similar in terms of length (25 mm), taper (6 or 8%) and tip diameter (0.25 mm):

* Conventional NiTi instrument (Protaper Universal F2®, Dentsply Maillefer, Ballaigues, Switzerland);
* "M-wire" instrument (Protaper Next X2®, Dentsply Maillefer, Ballaigues, Switzerland);
* "R Phase" instrument (K3XF®, SybronEndo, Orange, CA, USA);
* "CM wire" instrument (HyFlex®, Coltene Whaledent, Cuyahoga Falls, OH, USA).

2.2 Methodologies

2.2.1 Differential scanning calorimetry

Microstructural characterization of NiTi endodontic instruments has been performed using a differential scanning calorimetry (DSC Mettler Toledo DSC 822). Endodontic files were carefully cut using a low-speed diamond saw. Samples were placed in aluminium crucible with nitrogen gas flow environment. The thermograms were carried out in a range of temperature from + 70°C to -150°C with a heating or cooling rate of 5°C/min.
These results allow to identify the phase transformation temperatures and to calculate enthalpy changes (ΔH) associated with structural transition during heating.

2.2.2 Bending tests

The endodontic instrument flexibility was tested on a homemade cantilever bending apparatus [10]. The instruments are maintained at 45° relative to the 20 N measuring cell and bent from 0 to 5 mm. The device is placed in an enclosure filled with water maintained at the desired temperature by a thermostat for testing the files at different temperatures. The tests were performed at room temperature (24°C), temperature at which practitioners evaluate the flexibility and choose their endodontic instruments and at clinical use temperature (intra dental root, 37°C). The results are discussed only in a qualitative way because of the various geometry designs of the instruments (different cross sectional shape and taper).

3 Results

3.1 DSC

DSC thermograms of the different types of endodontic instruments are presented figure 1. The transformation sequences are very different from one sample to the other. For three of them (conventional, "M-wire" and "R phase" files), DSC curves showed two step transformations during cooling, the first exothermic peak corresponding to the transformation from austenite (A) to R-phase (R) and the second exothermic peak at lower temperature from R-phase to martensite (M). For conventional and "M-wire" samples, the second peak was broad and weak and dissimulated in the baseline of the thermogram. For these three files, two-step endothermic transformations, very close but distinct, occurred during heating, corresponding to the M→R and R→A reversion. For "CM wire" instrument, DSC cooling curve presented three step transformations: A→R followed by a weak peak corresponding to a first transformation to martensite (*M1) and a third peak corresponding to the formation of a second martensite M2 (better defined). On heating, only two transformation peaks can be distinguished.

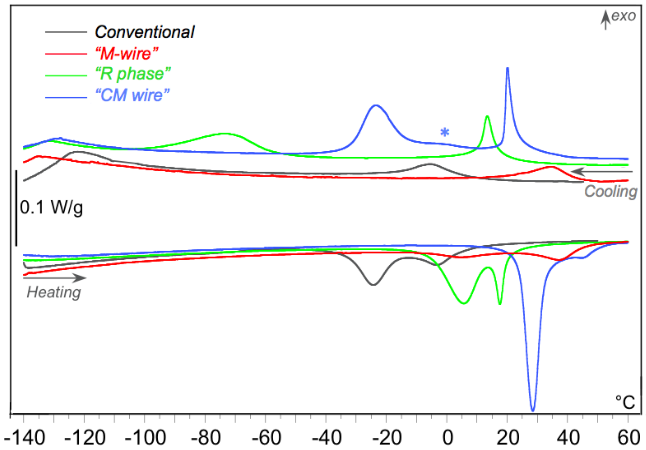

Figure 1. Superposition of DSC curves of endodontic files.

The transformation temperatures and enthalpy values were presented on the table 1 (cooling) and table 2 (heating).

Table 1. Cooling transformation temperatures.

Files	*Cooling*			
	R_s (°C)	R_f (°C)	M_s (°C)	M_f (°C)
Conventional	6.9	-19.54	-	-
"M-wire"	44.8	16.09	-	-
"R phase"	18.39	9.77	-56.32	-98.27
"CM wire"	24.13	18.42	-10.91	-32.75

Table 2. Heating transformation temperatures.

Files	*Heating*			
	R'_s (°C)	A_s (°C)	A_f (°C)	ΔH (J/g)
Conventional	-34.48	-	8,6	10.62
"M-wire"	-14.36	-	46.55	6.10
"R phase"	-5.74	-	20.68	15.63
"CM wire"	-	23.56	52.29	19.47

At ambient temperature, conventional and "R phase" samples were fully austenitic, "M-wire" was mainly in R-phase and austenite and "CM wire" was mainly in austenite with a little R-phase. It is expected that these two last instruments may also show martensite if they are strained.

At body temperature, conventional and “R phase” instruments were fully austenitic and “M-wire” file was half austenitic and half R-phase. “CM wire” sample was fully austenitic if it is not deformed but with strain, R-phase and martensite would also be present.

3.2. Bending tests

For each brand, three tests at least were performed on the same file to assess the reproducibility of results.
All the bending curves were similar (figures 2 and 3). At first and until 3 mm of deflection, only the tip of the instrument was bent. Between 3 and 5 mm, the curvature moves towards the middle of the file. Because only the apical third is concerned in most clinical situations, tests beyond 5 mm of deflection are considered not relevant for the present study.
All the recorded curves presented characteristics of superelastic behavior.

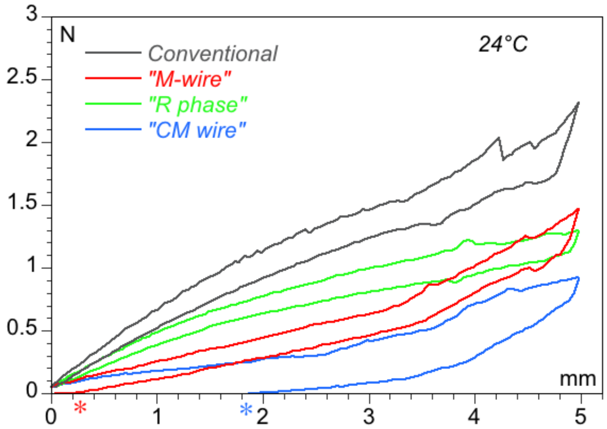

Figure 2. Bending curves of endodontic instruments at ambient temperature.

At room temperature (fig. 2), two files (“M-wire” and “CM wire”) did not recover their original shape.
At body temperature (fig. 3), all the files returned substantially to their initial form.

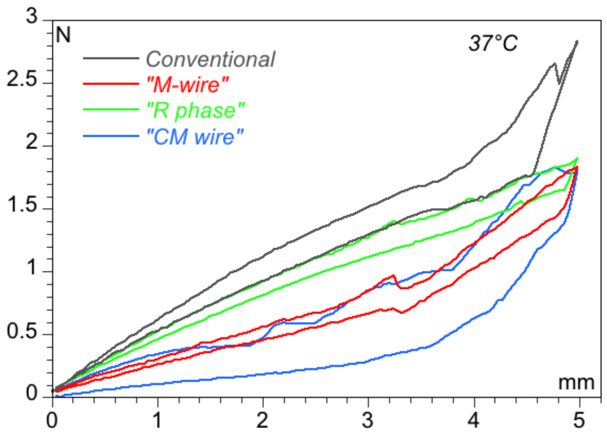

Figure 3. Bending curves of endodontic instruments at body temperature.

At room and body temperatures, all new generation instruments were more flexible than the conventional one. At 37°C compared to 24°C, the forces for 5 mm of deflection of all the files was increased more or less significantly between 21.4% for the conventional one and 112.6% for “CM wire” (table 3). Despite the different innovative thermomechanical treatments, the three new generation files bend to 5 mm with almost an equivalent force (~1.85 N, table 3).

Table 3. Forces (Newton) recorded for 5 mm bending at 24°C and 37°C and increasing between these temperatures (%).

Files	*Bending at 5 mm*		
	At 24°C (N)	At 37°C (N)	%
Convent.	2.3007 ± 0.0549	2.7930 ± 0.1542	21.4
“M-wire”	1.4203 ± 0.0482	1.8553 ± 0.0235	30.6
“R phase”	1.2820 ± 0.0070	1.8783 ± 0.0290	46.5
“CM wire”	0.8843 ± 0.0271	1.8797 ± 0.0300	112.6

4 Discussion

In the present study, differential scanning calorimetry is used to investigate the phase transformation temperatures of rotary endodontic instruments resulting from different thermomechanical treatments. All instruments have typical transformation sequences of NiTi alloys with three distinct crystallographic phases: austenite, R-phase and martensite. R-phase is present for all endodontic files and not just for the instruments named "R phase” technology. However, the characteristic curves of all the samples showed large differences from one instrument to another. The results of bending tests at different temperatures exhibit a marked temperature dependent stress-strain response (table 3), and are characteristic of the superelasticity (Clausius-Clapeyron relation). These tests clearly illustrate the phenomenon whereby the endodontic instrument becomes stiffer when the temperature increases and moves away from the transformation temperatures (R-phase and/or martensite). Finally, there are two mechanisms in competition that control the deformation of an endodontic file in a curved root canal: classical elasticity of austenite and/or R-phase and superelasticity (R-phase, martensite).

In 2007, the "M-wire” technology appears, it corresponds to a shaping process associating a cold drawing to heat treatments in order to obtain a two-phase alloy composed of martensite and phase-R at room temperature [11,12]. Compared to the conventional NiTi file, “M-Wire” sample showed higher transformation temperatures in agreement with results of several authors [12,13]. In previous work [10], we performed some thermal treatments on endodontic instruments to observe the changes in the mechanical properties and transformation characteristics: a thermal treatment at 400°C on a conventional NiTi file allowed us to achieve similar results. Ni-rich precipitations (Ti_3Ni_4) can form in the matrix with no real change in the dislocation density [14]. But, this precipitation depleted the matrix of nickel resulting in an increase of the transformation temperatures of the alloy, which become closer to the temperature of clinical use. This explained in part the increased flexibility of this instrument although this alloy is hardened. The DSC results allowed us to speculate on the flexural behavior of this endodontic file. At ambient temperature (fig. 1), martensite can remain after it was generated under stress and this fact explains that the file did not return to its initial shape after bending tests (fig. 2). At body temperature, "M-wire" instrument was half austenitic and half R-phase allowing it to take advantage of several mechanisms when it was bent: elasticity of austenite and R-phase (with lower elastic modulus), reorientation of the R-phase variants, stress-induced R-phase and martensite.

In 2008 a new file manufacturing protocol appears, the "R phase" technology. It would be a twisting method coupled to heat treatments. The goal would be to stabilize the R-phase at higher temperature. "R phase" instrument is probably made from Nitinol and fabricated by a grinding process followed by a special heat treatment to accommodate some of internal stresses caused by machining [6,15]. Compared with the conventional NiTi file, this instrument presents also higher transformation temperatures with an A_f temperature just below ambient temperature. In a previous work [10], thermal treatment at 510°C on a conventional NiTi file gave similar results. Such a heat treatment, by reducing the internal stresses and/or by partially dissolving the Ti_3Ni_4 precipitates, increases the mobility of R-phase or martensite interfaces, making phase transformations "easier" in the material. This is in agreement with the enthalpy value, which is higher than for the conventional endodontic file (table 2). At ambient and body temperatures, "R phase" instrument is fully austenitic but with R_s and A_f temperatures closer to 37°C (compared to the conventional NiTi file) allowing a superelastic behavior during clinical use. When the file is curved in a root canal, elasticity of austenite and stress-induced R-phase and/or martensite are responsible for its good flexibility.

In 2010, another manufacturing process appears, billed as more promising. This treatment is called "CM wire" by manufacturers for Controlled Memory wire. They have reported that this file may respond to pressure, torque and resistance with a lengthening of the spirals. Unlike conventional NiTi instruments, this can be reversed. During sterilization, the instruments can recover their initial shape [6]. Zhou et al [16] have investigated the starting wire blanks of "CM wire" files after thermal treatment and before machining. They indicated that the composition of "CM wire" and conventional files could be considered as the same whereas Zinelis et al. [17] found that this endodontic instrument exhibit a lower percentage of nickel (52.1 wt.%) than the other NiTi files. The reason is probably the machining process and the post-heat treatment, only difference between these two studies. Shen et al. [18] found that the finishing temperature of austenite transformation (A_f) and the phase transformation enthalpy changes were much higher than those of the conventional wires, which is in agreement with our results in the present study (table 2). In addition, their DSC curves also show three-stage phase transformation on cooling but they did no offer any explanation.

Three-stage martensitic transformation has already been described in aged Ni-rich NiTi alloys and various explanations have been proposed. According to Fan et al. [19], local inhomogeneity of the austenite phase around Ti_3Ni_4 precipitates is responsible for the three-stage transformation, behavior can be observed in samples that have been treated in the air or low vacuum atmosphere [20]. Such a transformation sequence would be due to preferential precipitation of Ti_3Ni_4 at grain boundary that generates a very significant heterogeneity in microstructure and chemical composition between grain boundary and interior. This phenomenon would explain the lower nickel concentration (the precipitates are rich in nickel and deplete the matrix) reported by some authors in the literature. Thus, we suggest that the sequence of transformation in "CM wire" instrument is as following: during cooling, the first peak corresponds to A→R transformation of grain boundary region (high density of precipitates) followed by A→M1 transformation (second peak) of the grain interior region (without particles) then R→M2 transformation (third peak) of grain boundary region; during heating, the first peak corresponds to M2→A transformation of the grain boundary region and then the second peak is M1→A transformation of the grain interior region. The reverse transformations did not go through the R-phase; martensite is transformed directly into austenite. Therefore, without strain, at ambient temperature, "CM wire" is mainly austenitic with little R-phase. When the file is curved, stress induced martensite and remains stable at this temperature (inferior to A_f). The instrument does not recover its original shape and remains deformed (figure 2). But at body temperature, this endodontic file is fully austenitic. When it is curved in a root canal, elasticity of austenite and/or R-phase, stress-induced R-phase and/or martensite and variant reorientation are responsible for its good flexibility.

According to the literature [6,15,18,21], all these new endodontic instruments exhibited better fatigue properties than the conventional file.

5 Conclusion

In recent years, several new manufacturing processes have been developed to optimize the microstructure of NiTi alloys, in particular, the development of new thermomechanical treatments named "M-wire", "R phase" and "CM wire" technologies. Innovative treatments would, according to the manufacturers, improve the flexibility of endodontic instruments and resistance to cyclic fatigue. All new instruments showed increased transformation temperatures and were more flexible than the conventional NiTi file. The greater flexibility of these instruments should be attributed to their lower initial apparent elastic modulus, which can be associated with the stress-induced reorientation of the R-phase and/or martensite (present in all instruments analyzed in this study and not only in the “R phase” sample). Although the exact thermomechanical history remains unknown, all the aforementioned data imply that the endodontic instruments are manufactured by cold work followed by heat treatments. The distribution of Ti_3Ni_4 precipitates influences the transformation temperatures. Finally, the manufacturers are trying to increase the transformation temperatures in order to reduce the stresses that will be exerted on the file in operation in order to improve the flexibility. This strategy implies to prefer the endodontic file to work in R-phase or martensite.

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