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# Heat Treatment of Dental Alloys: A Review

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Additional information is available at the end of the chapter

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## 1. Introduction

Metallic materials have widespread use in dentistry for clinical treatment and restoration of teeth. Major areas of usage are: (1) restorative dentistry and prosthodontics (dental amalgam and gold alloy restorations for single teeth, metallic restorations for multiple teeth, including metal-ceramic restorations, removable partial denture frameworks, and dental implants), (2) orthodontics (wires which provide the biomechanical force for tooth movement), and (3) endodontics (rotary and hand instruments for treatment of root canals). Heat treatment of the metal can be performed by the manufacturer, dental laboratory, or dentist to alter properties intentionally and improve clinical performance. Heat treatment of the metal also occurs during the normal sequence of preparing a metal-ceramic restoration, when dental porcelain is bonded to the underlying alloy substrate. Moreover, intraoral heat treatment of some metallic restorations occurs over long periods of time. There is an enormous scientific literature on the heat treatment of metals for dentistry. A search of the biomedical literature in May 2012, using PubMed [<http://www.ncbi.nlm.nih.gov/pubmed/>] revealed nearly 450 articles on heat treatment of dental alloys. The purpose of this chapter is to provide a review of the heat treatment of metallic dental materials in the foregoing important areas, describing the important property changes, with a focus on the underlying metallurgical principles.

## 2. Restorative dentistry and prosthodontics

### 2.1. Dental amalgams

Dental amalgams are prepared in the dental office by mixing particles of a silver-tin-copper alloy for dental amalgam that may contain other trace metals with liquid mercury. The initially mixed (termed triturated) material is in a moldable condition and is placed (termed condensed) directly by the dentist into the prepared tooth cavity, where it undergoes a setting process that produces multiple phases and can require up to one day for near

completion. Extensive information about the several different types of dental amalgams are provided in textbooks on dental materials [1,2]. Particles of the alloy for dental amalgam are manufactured by either lathe-cutting a cast ingot or directing the molten alloy through a special nozzle. Both the machining of the lathe-cut particles and the rapid solidification of the spherical particles create residual stress. In addition, the microstructure of the solidified silver-tin-copper alloy has substantial microsegregation. Consequently, manufacturers of the alloy powder for dental amalgam perform a proprietary heat treatment to relieve residual stresses and obtain a more homogeneous microstructure. This heat treatment is of considerable practical importance since it affects the setting time of the dental amalgam after the powder is mixed with mercury. Subsequently, the dental amalgam restorations undergo intraoral aging, which can be regarded as heat treatment, and detailed information about the microstructural phase changes for prolonged intraoral time periods has been obtained from clinically retrieved dental amalgam restorations [3].

## 2.2. Gold alloys for all-metal restorations

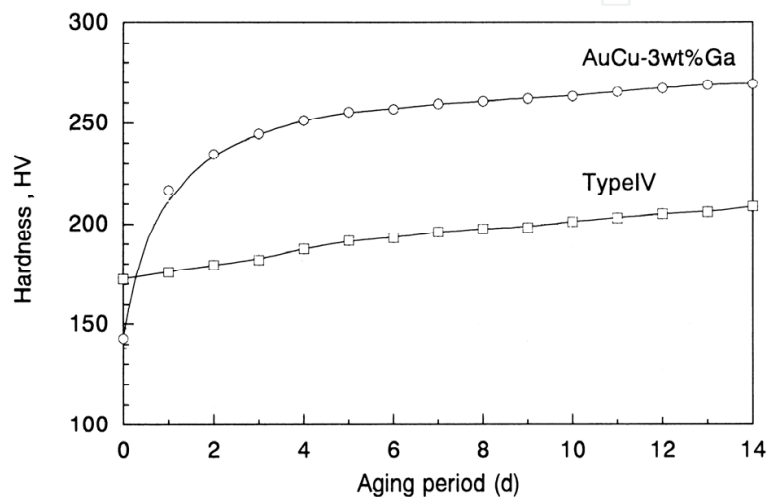
Gold alloys are principally used for all-metal restorations (inlays, crowns and onlays) in single posterior teeth. These alloys are cast by a precision investment process, and the restorations are cemented by the dentist into the prepared tooth cavity. The original gold casting alloys contained over approximately 70 wt.% gold, but the very high price of gold has led to the development of alloys that contain approximately 50 wt.% gold. These alloys also contain silver, copper, platinum, palladium, zinc, and other trace elements, including iridium for grain refinement. Information about the dental casting process and the gold alloys is available in dental materials textbooks [1,2]. Detailed compositions and mechanical properties of specific alloys are available on the website of the major manufacturers. Another valuable reference is the current ISO Standard on metallic materials for fixed and removable dental appliances [4], which stipulates mechanical property requirements. In the normal dental laboratory procedure, gold castings for all-metal restorations are water-quenched after solidification, following loss of the red heat appearance for the sprue. This results in formation of a disordered substitutional solid solution and leaves the alloy in the soft condition, which is preferable since adjustments are more easily made on the restoration by the dental laboratory or dentist. The gold alloy casting can also be placed in the soft condition by heating at 700°C for 15 minutes and water-quenching. The quenched gold casting may be placed in the hard condition by heat treatment at 350°C for 15 minutes and air-cooling. This heat treatment results in formation of ordered AuCu or AuCu<sub>3</sub> regions in the disordered matrix of the high-gold or lower-gold alloys, respectively. Examples of changes in clinically important mechanical properties from heat treatment are shown in Table 1 for two gold alloys, where (S) and (H) represent the soft and hard conditions.

In practice, dental laboratories do not perform heat treatments on the cast gold restorations because of the time involved. However, it appears to be fortunate that the gold alloys that contain sufficient copper to undergo ordering will undergo age hardening in the mouth.

Figure 1 compares the intraoral aging behavior of a traditional high-gold dental alloy (Type IV) and a special gold alloy containing gallium (AuCu-3wt%Ga) [5].

Alloy	Vickers Hardness		0.2% Offset Yield Strength		Percentage Elongation	
Firmilay (74.5% Au)	121 (S)	182 (H)	207 MPa (S)	276 MPa (H)	39% (S)	19% (H)
Midas (46% Au)	135 (S)	230 (H)	345 MPa (S)	579 MPa (H)	30% (S)	13% (H)

**Table 1.** Summary of property changes resulting from heat treatment of two gold alloys for all-metal restorations. [<http://www.jelenko.com/>, accessed August 15, 2012]



**Figure 1.** Comparison of the two-week aging behavior at 37°C for a high-gold dental alloy and a dental gold alloy containing gallium that was designed to undergo intraoral aging. From [5] and reproduced with permission.

### 2.3. Alloys for fixed prosthodontics (metal-ceramic restorations)

Metal-ceramic restorations are in widespread clinical use for restorative and prosthetic dentistry, and are employed for single-tooth restorations and for restorations involving multiple adjacent teeth (fixed prostheses or crown-and-bridgework). An alloy is cast using the precision investment procedure in dental laboratories to fit accurately to the prepared tooth or teeth, and to form a substrate (termed the coping) for the porcelain. After an initial oxidation step that forms a native oxide on the metal surface, one or two layers of opaque porcelain are bonded to the metal, followed by the application of a layer of body porcelain and a surface glaze [1,2]. In order to have a strong bond between the porcelain and metal, which is essential for clinical longevity of the metal-ceramic restoration, the coefficients of thermal contraction for the metal and porcelain must be closely matched, and a difference not exceeding 0.5 ppm/°C is generally desired. Mechanical property requirements for the alloys are stipulated in ANSI/ADA Specification No. 38 (ISO 9693) [6], and the minimum value of 250 MPa for the 0.2% offset yield strength is important, since the thin coping must withstand intraoral forces without undergoing permanent deformation. The metal-ceramic

bond strength (termed the bond compatibility index) is measured with a three-point bending test that uses thin cast alloy strip specimens having a centrally located area of sintered porcelain, and a minimum bond strength (shear stress) of 25 MPa is stipulated.

Both noble and base metal alloys are used for bonding to dental porcelain. The current American Dental Association classification has four alloy groups for fixed prosthodontics [7]: (1) high-noble (gold-platinum-palladium, gold-palladium-silver and gold-palladium); (2) noble (palladium-silver, palladium-copper-gallium, and palladium-gallium); (3) predominantly base metal (nickel-chromium and cobalt-chromium); (4) titanium and titanium alloys. Information about these alloys for metal-ceramic bonding is summarized in a textbook on fixed prosthodontics [8]. The principal mechanisms for metal-ceramic bonding are (a) mechanical interlocking from the initially viscous porcelain at the elevated sintering temperatures flowing into microirregularities on the air-abraded cast metal surface and (b) chemical bonding associated with an interfacial oxide layer between the metal and ceramic. These two mechanisms are evident from photomicrographs, found in numerous references [8], of the fracture surfaces for metal-ceramic specimens prepared from a wide variety of dental alloys. This native oxide forms on the cast alloy during the initial oxidation firing step in the dental porcelain furnace. Noble alloys for bonding to dental porcelain contain small amounts of secondary elements, such as tin, indium and iron, which form the native oxide and also increase the alloy strength. However, Mackert et al [9] found that during initial oxidation heat treatment, metallic Pd-Ag nodules formed on the surface of a palladium-silver alloy for metal-ceramic restorations and only internal oxidation occurred for the tin and indium present in the alloy composition. They concluded that porcelain bonding arose predominantly from mechanical interlocking with the nodules. Internal oxidation has also been reported for high-gold [10] and high-palladium [11] alloys for bonding to porcelain, but both alloy types also formed surface oxides [10,12].

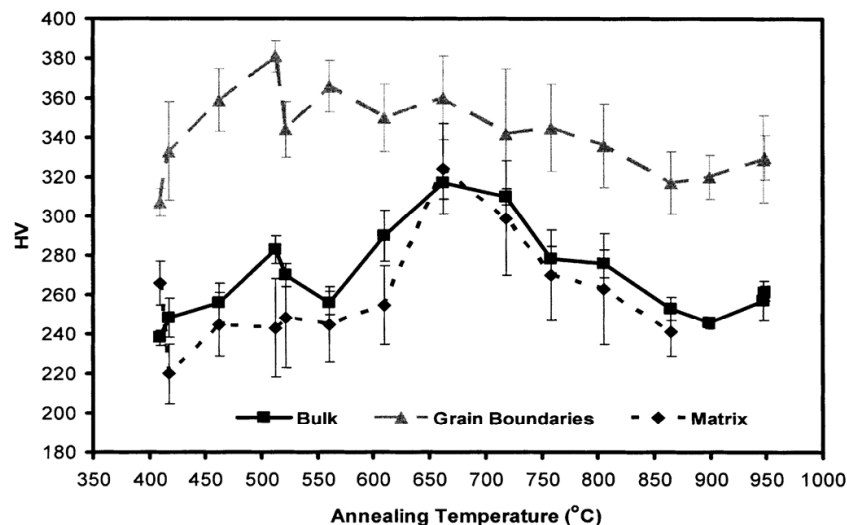
The initial oxidation step and subsequent sintering (also termed baking or firing) of the dental porcelain layers causes the alloy to experience substantial heat-treatment effects. Under normal dental laboratory conditions, the porcelain firing sequence is performed rapidly. For example, in one study heating of high-palladium alloys in the dental porcelain furnace was performed at approximately 30°C/min over a temperature range from 650°C to above 900°C, and the total heating time for the several firing cycles at these elevated temperatures was about 45 minutes [11]. Studies [13-15] have shown that the as-cast microstructures of noble metal alloys for bonding to porcelain are highly inhomogeneous in the initial as-cast condition, presumably from substantial elemental microsegregation that occurs during the rapid solidification involved with casting into much cooler investment [1,2]. After simulation of the dental porcelain firing sequence, the noble metal alloy microstructures become substantially homogeneous, and there are accompanying changes in the mechanical properties, as shown in Table 2.

Peaks in Vickers hardness for heat treatments at temperatures that span the porcelain-firing temperature range indicate that influential precipitation processes can occur in some noble alloys for fixed prosthodontics [13,16]. For the gold-palladium-silver alloy in Table 1,

heating an as-cast specimen to 980°C caused a pronounced decrease in Vickers hardness, and subsequent heat treatments at temperatures from 200° to 980°C revealed a pronounced peak in Vickers hardness at approximately 760°C. The absence of substantial changes in Vickers hardness for similar heat treatments of the gold-palladium alloy in Table 2 arises from differences in the precipitates that form in the two complex alloy compositions. Figure 2 presents the age hardening behavior of a palladium-silver alloy, where specimens were subjected to isothermal annealing for 30 minute time periods at temperatures from 400°C to 900°C that span the range for the porcelain firing cycles [16]. Bulk values of Vickers hardness were obtained with 1 kg loads, and 25 g loads were used to obtain hardness values for specific microstructural regions. In contrast, research suggests that microstructures of popular nickel-chromium base metal alloys used with dental porcelain are not changed substantially during dental laboratory processing [17].

Alloy Type	Vickers Hardness		0.2% Offset Yield Strength		Percentage Elongation	
Au-Pd-Ag (Neydium)	199 (C)	218 (P)	420 MPa (C)	490 MPa (F)	6% (C)	8% (F)
Au-Pd (Olympia)	213 (C)	225 (P)	500 MPa (C)	540 MPa (F)	13% (C)	20% (F)

**Table 2.** Mechanical properties for two noble metal alloy types used with dental porcelain, comparing the as-cast condition (C) and simulated porcelain firing heat treatment (F) [13].



**Figure 2.** Annealing behavior of a palladium-silver alloy for fixed prosthodontics, showing changes in Vickers hardness for a heat treatment temperature range that spans the porcelain firing cycles. Reproduced from [16] with permission.

## 2.4. Alloys for removable prosthodontics

Base metal casting alloys (nickel-chromium, cobalt-chromium and cobalt-chromium-nickel) are popular for fabricating the metallic frameworks for removable partial dentures because of their lower cost [1,2]. Once an active area of dental metallurgy research, studies have found that these alloys have dendritic microstructures in the as-cast condition, because of



the absence of suitable grain-refining elements, and that heat treatment is ineffective for producing improved mechanical properties [18]. A more recent publication shows the dendritic microstructures of some current alloys and their mechanical properties [19].

Removable partial denture frameworks have clasps that engage the teeth. These clasps can be cast as part of the entire framework, or alternatively wire clasps can be joined to the cast framework in the dental laboratory [1,2]. Both noble metal and base metal wires for clasps are available [20]. Because of their superior strength compared to the cast base metal alloys, wire clasps with smaller cross-section dimensions can be used with the frameworks, but caution is required during joining in the dental laboratory to avoid overheating that will cause loss of the wrought microstructure. Wire clasps are used in the as-received condition; heat treatment is not recommended before joining to the framework.

## 2.5. Dental implant alloys

Dental implants in current widespread clinical use are manufactured from CP (commercially pure) titanium or Ti-6Al-4V, and some implants have a thin bioceramic surface coating (typically hydroxyapatite, the principal inorganic constituent of bone and tooth structure). Proprietary heat treatments [21] are performed on Ti-6Al-4V by manufacturers to obtain optimum microstructures for the implants; minimal information is currently available about these microstructures in the dental scientific literature.

Recently, there has been considerable research interest in the development of new titanium implant alloys for orthopedic applications that have improved biocompatibility compared to the Ti-6Al-4V alloy in widespread current use. There is particular interest in the beta-titanium alloys which have lower elastic modulus than Ti-6Al-4V to minimize stress shielding and subsequent loss of the surrounding bone which has a much lower elastic modulus. Stress shielding does not seem to be of concern for dental implants, presumably because of the threaded designs. Biocompatible titanium-niobium-zirconium beta alloys have been investigated, and oxide nanotubes can be grown on the alloy surface by an anodization technique, and subsequent heat treatment can be employed to modify the structure of the nanotubes [22]. In another exciting research area, titanium oxide nanowires have been recently grown on both CP titanium and Ti-6Al-4V using special elevated-temperature oxidation heat treatments in an argon atmosphere with low oxygen concentrations [23]. Both of these special types of surface oxide layers may prove to be useful for dental and orthopedic implants, but future testing in animals will be needed to examine their efficacy.

## 3. Orthodontics

### 3.1. Background

Orthodontic wires engaged in brackets that are bonded to teeth, after being deformed elastically during initial placement, provide the biomechanical force for tooth movement during unloading. There are four wire types in current clinical practice: stainless steel, cobalt-chromium, beta-titanium and nickel-titanium [24]. The clinically important

mechanical properties are (a) elastic modulus, which is proportional to the biomechanical force when wires of similar dimensions are compared; (b) springback, which is generally expressed as the quotient of yield strength and elastic modulus ( $YS/E$ ), and represents the approximate strain at the end of the clinically important elastic range; and (c) modulus of resilience, expressed as  $YS^2/2E$  and representing the spring energy available for tooth movement. (The permanent deformation portion of orthodontic wire activation is ineffective for tooth movement.) Round orthodontic wires are manufactured by a proprietary drawing sequence that involves several stages with intermediate annealing heat treatments. Rectangular orthodontic wires are manufactured by a rolling process utilizing a Turk's head apparatus. The wire drawing process with the heat treatments greatly affects mechanical properties.

### 3.2. Stainless steel orthodontic wires

A recent study that investigated stainless steel wires used in orthodontic practice found that most products were AISI Type 304 and that AISI Type 316L (low carbon) and nickel-free ASTM Type F2229 were also available [25]. While standard physical metallurgy textbooks consider the elastic modulus to be a structure-insensitive property, research has shown that the permanent deformation and heat treatments involved with the wire drawing process can substantially affect the elastic modulus of stainless steel orthodontic wires [26,27]. X-ray diffraction has revealed that conventional orthodontic wires manufactured from AISI Types 302 and 304, while predominantly austenitic structure, can contain the  $\alpha'$  martensitic phase, depending upon the carbon content and temperatures involved with the processing [28]. The presence of this martensitic phase accounts for the reduction in elastic modulus for some conventional stainless steel orthodontic wires. In addition, when fabricating complex stainless steel appliances, it is recommended that orthodontists perform a stress-relief heat treatment to prevent fracture during manipulation; a heating time up to 15 minutes and a temperature range of 300° to 500°C appears to be acceptable [29-31]. Heating austenitic stainless steel to temperatures between 400° and 900°C can result in chromium carbide precipitation at grain boundaries and cause the alloy to become susceptible to intergranular corrosion, and heating of austenitic stainless steel wires above 650°C should not be done because loss of the wrought microstructure causes degradation of mechanical properties.

### 3.3. Cobalt-chromium orthodontic wires

The cobalt-chromium orthodontic wire (Elgiloy) marketed by Rocky Mountain Orthodontics (Denver, CO, USA) contains 40% Co, 20% Cr, 15.81% Fe, 15% Ni, 7% Mo, 2% Mn, 0.15% C carbon and 0.04% Be beryllium (<https://www.rmortho.com/>, accessed August 15, 2012). Four different tempers (spring quality) are available, and the soft Blue temper is favored by many orthodontists because the wire is easily manipulated in the as-received condition, and then heat treated to increase the yield strength and modulus of resilience. Heat treatment (not recommended for the most resilient temper) is conveniently performed



with the electrical resistance welding apparatus commonly used in orthodontic practice, and the manufacturer provides a special paste that indicates when the heat treatment is complete. Alternatively, furnace heat treatment performed at 480°C for 5 minutes has been found to give satisfactory results [32]. An extensive study employing furnace heat treatment (480°C for 10 minutes) for three tempers and numerous sizes of the Elgiloy wires observed increases of 10% – 20% in elastic modulus and 10% – 20% in 0.1% offset yield strength, which resulted in substantial improvement of the modulus of resilience [27]. These changes in mechanical properties arise from complex precipitation processes during heat treatment that are not understood. Many other companies now market cobalt-chromium orthodontic wires, but studies of their mechanical properties and the results of heat treatment have not been reported.

### **3.4. Beta-titanium and other titanium-based orthodontic wires**

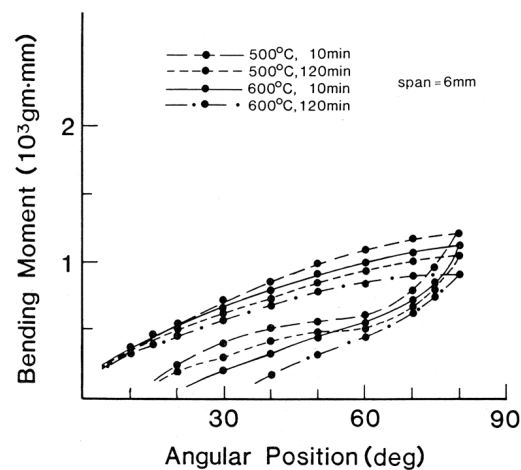
Beta-titanium orthodontic wires have the advantages of: (a) known biocompatibility from the absence of nickel in the alloy composition; (b) lower elastic modulus than stainless steel and cobalt-chromium wires, which provides more desirable lower orthodontic force for tooth movement; (c) higher springback than stainless steel and cobalt-chromium wires, which is desirable for the archwire to have greater elastic range; and (d) high formability and weldability, which are needed for fabrication of certain appliances [24]. A recent study [25] of commercially available titanium-based orthodontic wires revealed that most products are Beta III alloys [21] containing approximately 11.5 Mo, 6 Zr, and 4.5 Sn, similar to the original beta-titanium wire introduced to orthodontics [33,34]. Beta C [21] and Ti-45Nb beta-titanium and Ti-6Al-4V (alpha-beta) wire products are also available [25]. Heat treatment is not performed by the orthodontist on these wires, but care with the wire drawing and intermediate heat treatments by the manufacturer are essential for obtaining the desired mechanical properties. These processes must be conducted under well-controlled conditions because of the highly reactive nature of titanium.

### **3.5. Nickel-titanium orthodontic wires**

Following the pioneering work of Andreasen and his colleagues [35,36], near-equiatomic nickel-titanium (NiTi) wire was introduced to orthodontics by the Unitek Corporation (now 3M Unitek) [37]. This wire had the advantages of a much lower elastic modulus than the stainless steel and cobalt-chromium wires available at the time and a very large elastic range. The clinical disadvantage is that substantial permanent deformation of this wire is not possible to obtain certain orthodontic appliances that can be fabricated with the three preceding, highly formable, alloys. The original nickel-titanium wire had a work-hardened martensitic structure and did not exhibit the superelastic behavior (termed pseudoelasticity in engineering materials science) or the true shape memory characteristics displayed by subsequently introduced NiTi wires [1,38-41]. These nickel-titanium wires have been a very active area of research.

The mechanical properties of the nickel-titanium orthodontic wires are determined by the proportions and character of three microstructural phases: (a) austenite, which occurs under conditions of high temperature and low stress; (b) martensite, which occurs under conditions of low temperature and high stress; and (c) R-phase, which forms as an intermediate phase during the transformation between martensite and austenite. Very careful control of the wire processing and associated heat treatments, along with precise compositional control, by the manufacturer are needed to produce nickel-titanium wires with the desired superelastic, nonsuperelastic, or shape memory character [42,43].

Heat treatments have been exploited by manufacturers to control the orthodontic force ranges produced by nickel-titanium archwires [39]. Heat treatment temperatures have ranged from 400° to 600°C with times from 5 minutes to 2 hours [39,40]. Effects of heat treatment on cantilever bending plots for two sizes of a round superelastic nickel-titanium wire are presented in Figure 3 [40].

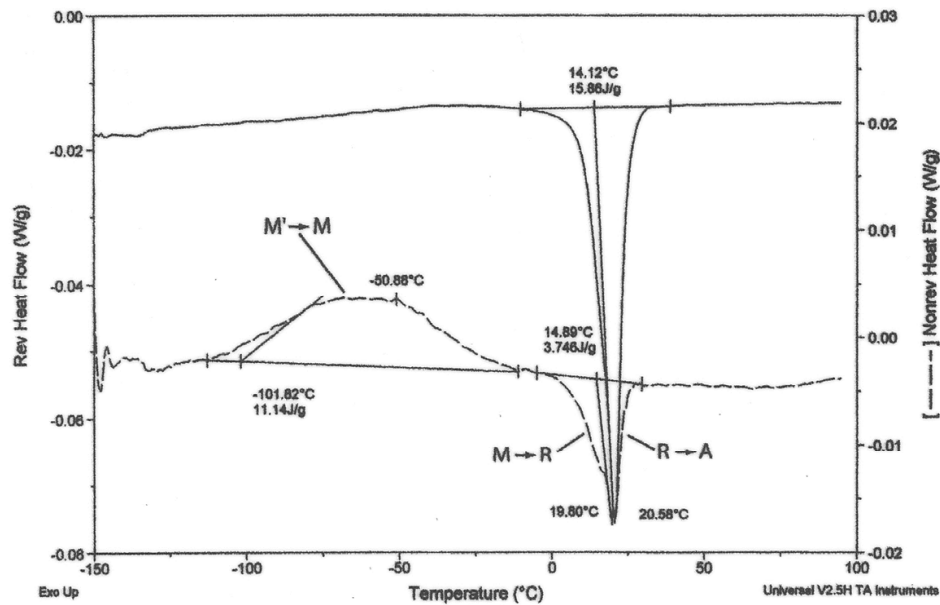


**Figure 3.** Effects of heat treatments on cantilever bending plots for 6 mm test spans of a superelastic nickel-titanium orthodontic wire. Reproduced from [40] with permission.

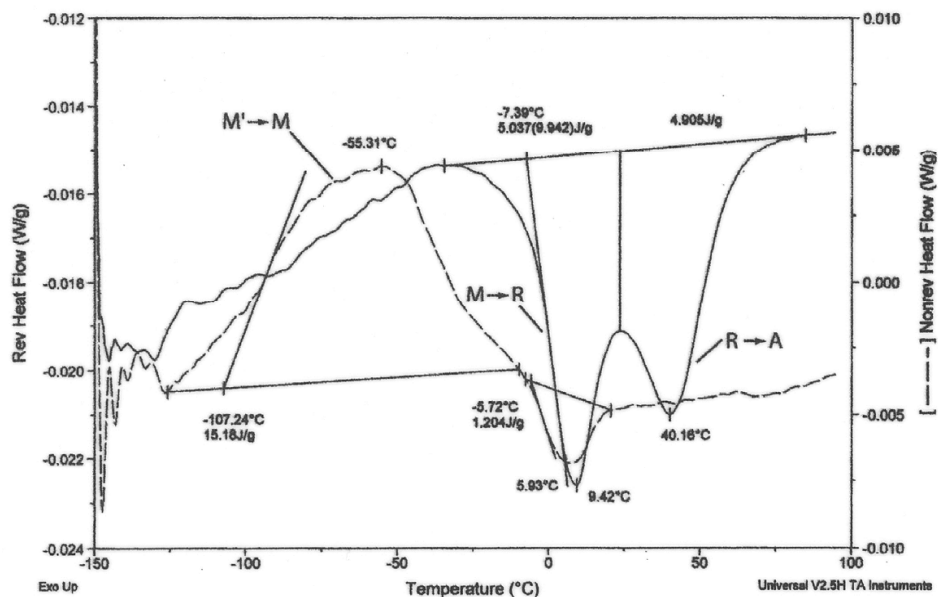
Loss of superelastic behavior occurs for the 2 hour heat treatment at 600°C, evidenced by the large decrease in springback (difference between the original deflection of 80 degrees and the final angular position on unloading). Heat treatment at 500°C for 10 minutes had minimal effect, while heat treatment for 2 hours caused a decrease in the average superelastic bending moment during the unloading region of clinical importance. Bending properties for nonsuperelastic wires were only slightly affected by these heat treatments. In addition to the use of furnace heat treatment, electrical resistance heat treatment [44] has also been exploited by one manufacturer to produce archwires where the level of biomechanical force varies with position along the wire [24].

Microstructural phases at varying temperatures in nickel-titanium orthodontic wires and their transformations are conveniently studied by differential scanning calorimetry (DSC) [45]. Temperature-modulated DSC provides greater insight into the transformations than conventional DSC [46]. Figures 4 and 5 present temperature-modulated DSC heating curves for shape memory and superelastic nickel-titanium orthodontic wires, respectively. The

transformations involving austenite (A), martensite (M) and R-phase (R) are labeled. The austenite-finish ( $A_f$ ) temperature for completion of the transformation from martensite to austenite on heating is determined by the intersection with the adjacent baseline of a tangent line to the peak for the final transformation to austenite [47].



**Figure 4.** Heating temperature-modulated DSC plot for a shape memory nickel-titanium orthodontic wire. Reproduced from [46] with permission.



**Figure 5.** Heating temperature-modulated DSC plot for a superelastic nickel-titanium orthodontic wire. Reproduced from [46] with permission.

The  $A_f$  temperature is below body temperature ( $37^\circ\text{C}$ ) for nickel-titanium wires that exhibit shape memory in the oral environment. The superelastic nickel-titanium wires have  $A_f$  temperatures that are greater than mouth temperature and have more widely separated

peaks for the successive transformations from  $M \rightarrow R$  and  $R \rightarrow A$ . The nonsuperelastic wires have much weaker transformations (lower values of enthalpy  $[\Delta H]$ ) and  $A_f$  temperatures that are also greater than mouth temperature [45]. Examination of x-ray diffraction patterns for nickel-titanium orthodontic wires revealed the effects of heat treatment on the  $M_s$  temperature for the start of the cooling transformation to martensite as well as the occurrence of stress relief and perhaps some recrystallization [24,48].

Transformation of a low temperature martensite phase ( $M'$ ) to the higher temperature form of martensite ( $M$ ), shown in Figures 5 and 6, is readily detected as a large exothermic peak on the nonreversing heat flow curves from temperature-modulated DSC. Transmission electron microscopy has revealed that this transformation arise from low-temperature twinning within the martensite structure [49].

## 4. Endodontics

### 4.1. Stainless steel instruments

Traditionally, endodontic treatment was performed with stainless steel hand files and reamers to remove the injured or diseased dental pulp from the root canals of teeth. While conventional elevated-temperature heat treatment is not recommended for these instruments, they are subjected to sterilization procedures before being using again with a different patient. One study found that dry heat sterilization (180°C for 2 hours) and autoclave sterilization (220 kPa pressure and 136°C for 10 minutes) slightly decreased the flexibility and resistance to torsional fracture of the instruments but they still satisfied the requirements for minimum angular deflection in the ISO standard [50]. Further research is needed to gain insight into the metallurgical origins of the property changes.

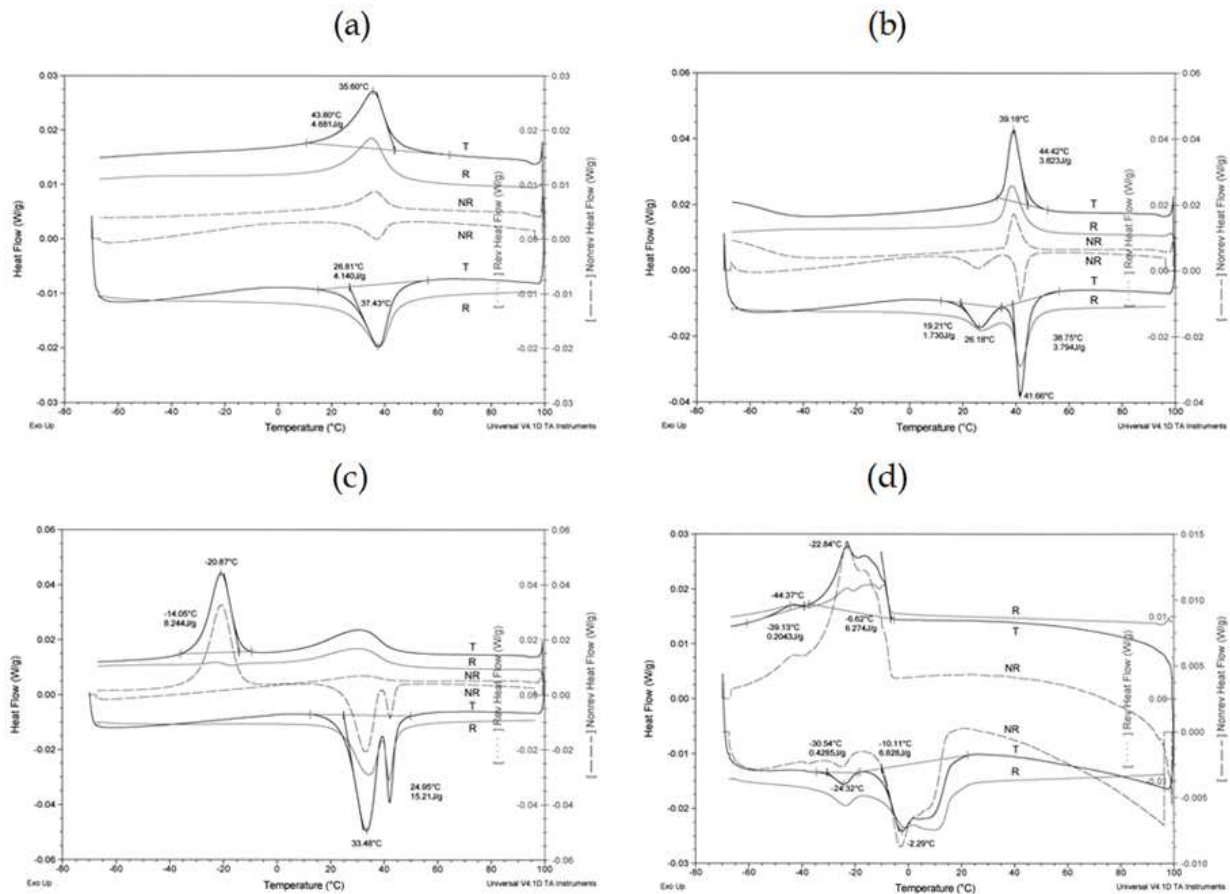
### 4.2. Nickel-titanium instruments

Following the pioneering work of Walia et al that introduced the nickel-titanium hand file to the endodontics profession [51], engine-driven rotary instruments were introduced that enable rapid instrumentation of root canals. These instruments are in widespread clinical use, and research on the nickel-titanium files has been a highly intensive area of research.

The major mechanical property of the equiatomic nickel-titanium alloy that led to replacement of the traditional austenitic stainless steel files was the much lower elastic modulus of NiTi, which enabled curved root canals to be negotiated with facility. An excellent review article [52] describes the manufacturing process for the nickel-titanium files, which are generally machined from starting wire blanks. The conventional nickel-titanium rotary instruments have been fabricated from superelastic nickel-titanium blanks.

Defects caused by the machining process and metallurgical flaws in the starting blanks, along with inadvertent overloading by the clinician, can result in fracture of the file within the root canal, which causes considerable patient anguish since the broken fragments often cannot be easily retrieved [53,54].

A recent study investigated the effect of heat treatment on conventional nickel-titanium rotary instruments, using temperature-modulated DSC and Micro-X-ray diffraction [55]. Results are shown in Figure 6 (a) – (d) for heat treatment at temperatures from 400° to 800°C in a flowing nitrogen atmosphere.



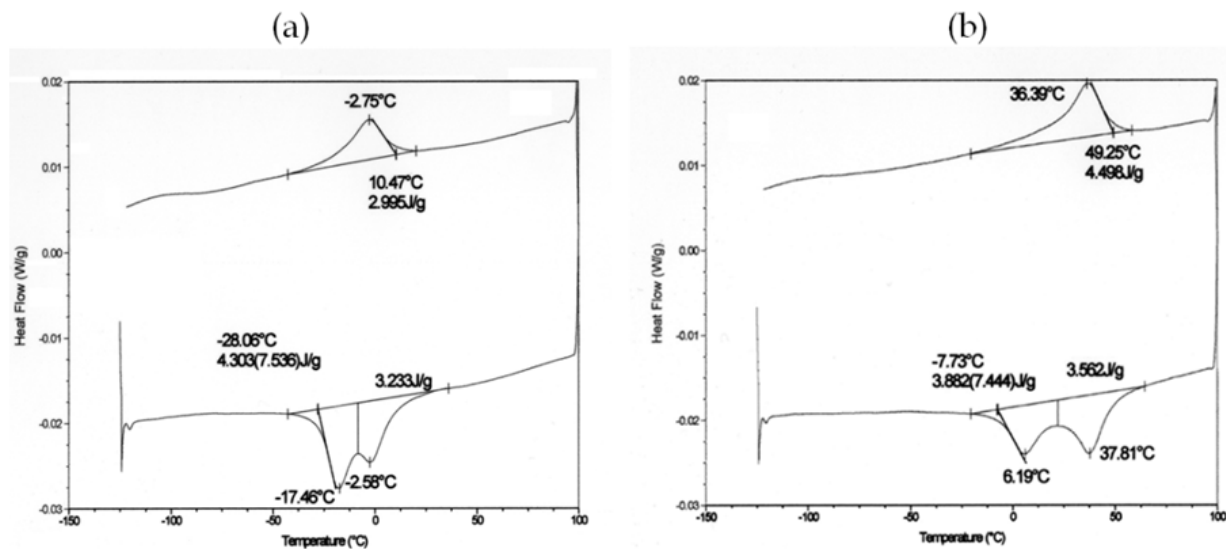
**Figure 6.** Temperature-modulated DSC reversing (R), nonreversing (NR) and total (T) heat flow curves for specimens from conventional rotary endodontic instruments after heat treatment in flowing nitrogen for 15 minutes at (a) 400°, (b) 500°, (c) 600° and (d) 850°C. From [55] and reproduced with permission.

Heat treatment between 400° and 600°C increased the  $A_f$  temperature for as-received conventional NiTi rotary instruments to approximately 45° – 50°C, and the transformations between martensite and austenite were changed to a more reversing character than nonreversing character [55]. Heat treatment in a nitrogen atmosphere might lead to a harder surface from the formation of nitrides [56], which is beneficial for cutting efficiency of the rotary instrument. This research suggested that heat treatment at temperatures near 500°C in a nitrogen atmosphere might yield the optimum microstructure and mechanical properties, with improved resistance to deformation and fracture for conventional NiTi rotary instruments. Heat treatment at temperatures exceeding 600°C should not be performed, since the superelastic behavior is lost along with potential degradation of the wrought microstructure [24]. Another study has reported that heat treatment at 430° and 440°C greatly improved the fatigue resistance of one conventional rotary instrument product [57].



New nickel-titanium rotary instruments have been marketed, for which the wire blanks were improved by special proprietary processing techniques, including heat treatment. The first notable example was M-Wire, named for its stable martensitic structure [58]. Previous conventional rotary instruments were fabricated from superelastic wire blanks with evident transformable austenite detected by conventional DSC [59]. However, when the conventional instruments were cooled far below room temperature to attain the fully martensite condition, the enthalpy changes for transformations from martensite to austenite were far below those for superelastic orthodontic wires [44,45], indicating that these instruments contain a substantial proportion of stable martensite in their microstructures.

Two different batches of M-Wire (termed Type 1 and Type 2), with unknown differences in proprietary processing, were obtained for characterization by temperature-modulated DSC and Micro-X-ray diffraction [58]. Figure 7 shows the differences in the temperature-modulated DSC plots for (a) conventional superelastic wire and (b) Type 1 M-Wire.



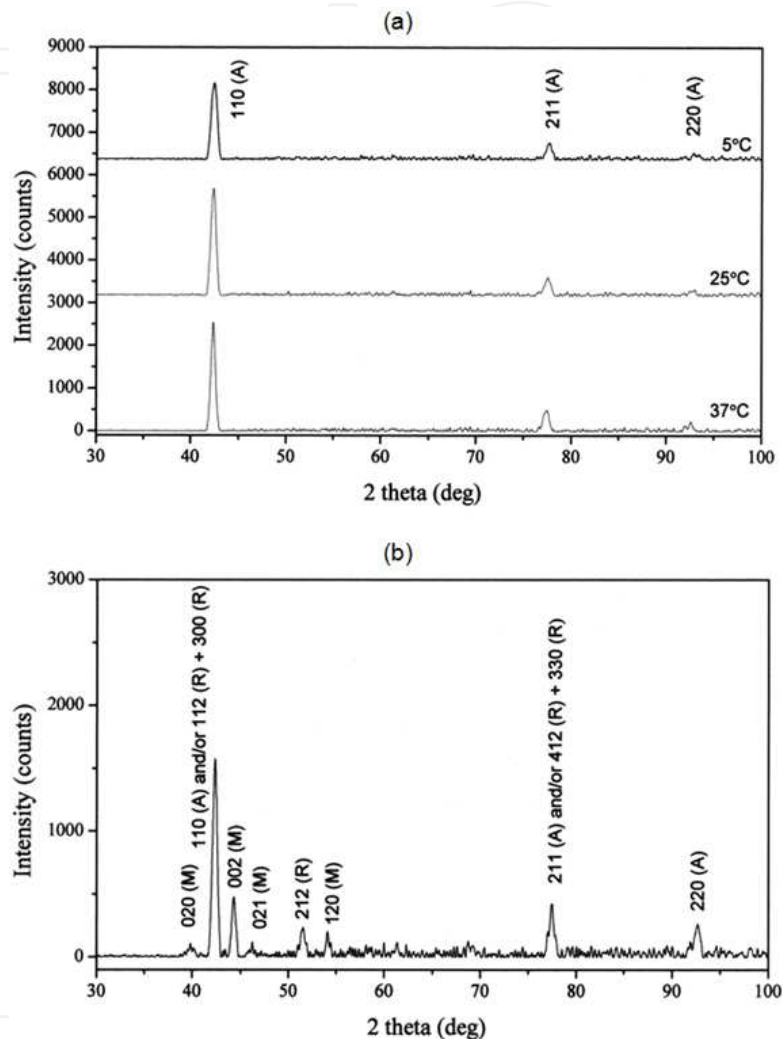
**Figure 7.** Comparison of temperature-modulated DSC total heat flow for (a) conventional superelastic wire and (b) Type 1 M-Wire. Lower curves are the plots for the heating cycles. Reproduced from [58] with permission.

The general appearances of the temperature-modulated DSC plots in Figure 7 (a) and (b) are similar. However, the approximate  $A_f$  temperatures for the conventional superelastic wire and Type 1 M-Wire were approximately 15°C and 50°C, respectively. The approximate  $A_f$  temperature for the Type 2 M-Wire was 45°C. The proportions of the different NiTi phases were quite different for Type 1 and Type 2 M-Wire, as shown in Figure 8.

The Micro-X-ray diffraction pattern indicated that Type 1 M-Wire had an austenitic structure, and the Micro-X-ray diffraction pattern from the conventional superelastic wire was similar. In contrast, the Micro-X-ray diffraction pattern from Type 2 M-Wire contained additional peaks for martensite and R-phase, along with peaks for austenite. However, when M-Wire was examined by transmission electron microscopy, a heavily deformed martensitic structure was found [58]. The explanation is that the DSC peaks only reveal NiTi



phases that are capable of undergoing transformation and that (stable) heavily deformed martensitic NiTi only produces weak x-ray diffraction peaks. Rotary instruments fabricated from M-Wire have been found to have similar  $A_f$  values, microstructures and Vickers hardness, so the machining process and other proprietary fabrication steps do not appear to markedly alter the inherent structure and properties of the starting blanks [60].



**Figure 8.** Micro-X-ray diffraction patterns for (a) Type 1 M-Wire and (b) Type 2 M-Wire. Peaks for austenite (A), martensite (M) and R-phase (R) are labeled. Reproduced from [58] with permission.

Recently, new nickel-titanium rotary instruments have been introduced, in which the wire blank is heated to an appropriate temperature for transformation to the R-phase and twisted, along with repeated heat treatment and other subsequent thermal processing; instruments have been characterized by conventional DSC and cantilever bending tests [61]. Another recent study has characterized several new nickel-titanium rotary instruments by DSC and conventional x-ray diffraction, along with optical and scanning electron microscopic examination of their microstructures, including use of energy-dispersive x-ray spectroscopic analyses (SEM/EDS), to investigate the martensitic microstructures and composition of precipitates [62]. Because of the potentially great commercial importance,

development of new rotary instruments with improved clinical performance is expected to remain an area of intensive research, along with study of the role of heat treatment [63].

It is essential to appreciate the complexity of the physical metallurgy of the nickel-titanium alloys and the effects of the severe thermomechanical processing of the starting wire blanks, along with heat treatments and machining of the wire blanks, on the metallurgical structure. Transmission electron microscopy and electron diffraction remain the best techniques to gain insight into the instrument microstructures and elucidate the relationships with mechanical properties and clinical performance.

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