PHYSICOCHEMICAL RESEARCH OF CLINICALLY RETRIEVED CU-NI-TI ORTHODONTIC ARCHWIRES

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Abstract. In modern orthodontics, thermally activated archwires are used more widely in clinical practice, because they have unique properties like superelasticity and biocompatibility. The aim of the present study was to characterize commercial 35° C Cu-NiTi archwires in terms of their phase transition behavior, chemical composition, surface topography properties after clinical usage, as well as the influence of the autoclaving process. **Materials and methods.** 35° C Thermo-Active Copper NiTi (CuNiTi) of ORM-CO, Glendora, CA, USA (as-received, as-received autoclaved and clinically retrieved) with rectangular cross-section and dimension 0.016x0.022 inch, were investigated. The physicochemical research was conducted via Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDX) and X-ray Diffraction Analysis (XRD). The autoclaving was done in Runyes model B autoclave. **Results.** The DSC results revealed the austenite start (9.8° C; 26.47° C) and austenite finish (28° C; 31.74° C) temperatures for the as-received and autoclaved archwires respectively. For clinically retrieved samples the austenite finish temperature (Af) is around 27° C. The XRD patterns of the as-received and clinically retrieved samples show almost identical diffraction patterns. Rough surface of the CuNiTi alloy was revealed by the SEM analysis. Autoclaving process seems to have no effects on archwires' structure and chemical composition. Chemical content of the investigated as-received CuNiTi are Ni, Ti and Cu: 47.07 wt% and 46.81 wt% and 6.11 wt%, respectively. The autoclaving process seems to have little influence on the transition temperature. The results from our study showed little difference (~7 °C) in the finish transition temperatures (Af), compared to the manufacturer's claim. No intermediate R phase was detected by DSC. **Conclusion.** A good knowledge of the structural changes that occur in CuNiTi alloys in the oral cavity is useful for the orthodontists in order to optimize orthodontic treatment.

Key words: 35 °C Thermo-Active Copper NiTi (CuNiTi), Autoclaving process, DSC, XRD, SEM, EDX

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INTRODUCTION

The thermoactivated NiTi alloys are introduced for use in orthodontics by ORMCO in 1994 and are classified as active martensitic alloys that feature thermally induced memory effect. The shape memory effect is characterized by the ability of the material to return to its original shape by heating the material above the transition temperature. The NiTi alloy's transition temperature from martensite to austenite occurs near the temperature of the oral cavity [1]. The transition between these two phases/structures is fully reversible, occurs at low temperatures and it takes place rapidly over some temperature transformation range (TTR). An intermediate phase, termed R-phase from its rhombohedral atomic arrangement, can form during the forward (heating) transformation from martensite to austenite and the reverse (cooling) transformation from austenite to martensite [2]. These different phases are responsible for two clinically significant properties of nickel-titanium: shape memory and superelasticity [3].

When the practitioner takes the wire at 25° C (room temperature) its modulus of elasticity is 44.9 GPa, but in the oral cavity, at 34° C, the modulus becomes 58.6 GPa. When the patient drinks hot coffee at 60° C, the modulus raises to 63.6 GPa [4]. Different elasticity allows the orthodontist to insert the archwire easier into the bracket slot of the misaligned teeth, since the archwire is in martensitic phase. These features of the CuNiTi archwires are very useful in the initial stages of treatment with fixed appliances. Many orthodontic companies claim that manufacturing process of copper-nickel-titanium gives the opportunity for production of archwires with more consistent transition temperatures, allowing the orthodontist to customize treatment to various patients based on the force level needed [5]. Some studies have shown that CuNiTi archwires with different transformation temperatures are marketed to provide differing force levels depending upon the temperature of the oral environment [5]. However, other studies showed no difference between as-received and clinically retrieved wires, except for a significant reduction in the heating enthalpy associated with the martensite to austenite transition in the 27° C and 35 °C CuNiTi archwires [6]. The clinically relevant benefits of CuNiTi over NiTi wires include more constant force generation over longer activation spans, greater resistance to permanent deformation, more stable superelasticity characteristics when cyclically loaded, better spring-back and less

hysteresis [7]. Brantley et al [8] speculated that some transformation in NiTi based wires may not be completely reversible on atomic level, possibly leading to structural defects and decreased clinical performance.

ORMCO's archwires are available at different temperature variants of 27° C, 35 °C, and 40° C, corresponding to their austenite finish temperatures (Af) for the completion of the martensite to austenite phase transformation [9]. Recent studies for Cu-NiTi archwires [10] (ORMCO, Glendora, CA, USA) claim that the archwires are in fully austenite phase in room temperature and with elemental composition as follows: 48.75 wt% nickel, 45.18 wt% titanium, 5.51 wt% copper and presence of 0.23 wt% chromium. Other studies show that 35° C CuNiTi wires are martensitic at room temperature (21 °C) and change into austenite when warmed in the oral environment (37° C) [6]. Moore et al [9] found that usually the temperature in the oral cavity is in the range of 33° C to 37° C for 79% of the time the archwire is in the mouth. They also state that 20% of the time, the temperature is lower than the average in the oral cavity 35° C and higher at 1% of the cases. Before placing the wire in the patient's mouth, some clinicians are using autoclaving process on the archwires so they can avoid infections in order to provide safety for their patients [5]. Autoclaving is a process of sterilizing materials and instruments with water vapor under pressure, which is done in appliances called autoclaves. Studies on the effect of autoclaving process on orthodontic wires have been going on since the 1980's and it is believed that this process can influence the properties of the orthodontic wires. There is a study from 2019 that investigated thermally activated NiTi archwires from different manufacturers, some of which are ORMCO's as-received, clinically used and clinically used sterilized CuNiTi wires. Those archwires have been studied only by DSC and the results did not show large variations in their transition temperature range [11]. The results are in contradiction with one another. Some of the studies report mechanical alterations, whereas others defend the opposite [12].

The aim of this study is to characterize commercial 35° C Thermo-Active Copper NiTi archwires (as-received, as-received autoclaved and clinically retrieved) in terms of their thermal behavior, chemical composition, surface topography properties and the influence of autoclaving process.

MATERIALS AND METHODS

Orthodontic CuNiTi archwires (ORMCO Glendora, CA, USA) from the same box (there are 10 packages in one box), provided from distributor, with transition temperature A_f at 35° C were examined at the areas corresponding to premolars. The experimental samples are with dimensions (0.016 x 0.022 inch) and rectangular cross-section. The investigations were conducted on as-received and clinically retrieved archwires as well as on one as-received archwire, gone through an autoclaving process.

In the beginning, the archwires are removed from the package and then placed in the patient's mouth. These wires were not previously autoclaved. The surface of the clinically retrieved archwires is initially treated with oxygen water and then with 70% ethyl alcohol. All patients were treated in the practice of researchers at the Department of Orthodontics in Sofia, Bulgaria.

Each sample was weighed before the analysis. The Differential Scanning Calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC model P-E 8000. For each individual test, before introducing the sample in the DSC apparatus, a calibration with indium was made. The reference chamber and each wire specimen were scanned at the temperature range from -50° C to +50° C (apparatus temperature range: from -170° C to +600° C) for both the heating and cooling processes, at 10° C/min. The DSC plots were qualitatively and quantitatively analyzed by the DSC manufacturer's software. Onset and Endset temperatures of the martensitic and austenitic phases were derived from the graphs produced by the software according to standard transition temperature determination methods.

The crystalline structure was studied at room temperature by a Bruker D8 Advance powder diffractometer with a Cu-K α target radiation at 40 kV and 20 mA, with a LynxEye Detector, within the range from 5-80° 2 θ at a constant step 0.02° 2 θ .

The surface morphology of the orthodontic archwires was studied by a Zeiss scanning electron microscope, model EVO MA-15 with LaB6 cathode. The accelerating voltage range of the apparatus used for the tests is from 0.2 to 30 kV. The research was conducted at 20 kV. The elemental composition of the samples was analysed by Energy Dispersive X-ray Spectroscopy (EDX) with Bruker Esprit 1.8 system at 20 kV accelerating voltage. The relative error of the

analysis in determining the elemental composition percentage by weight is 0.8%.

The program in which examined archwires were autoclaved is 121° C and a pressure of 1-1,3 bar. The full automatic cycle lasts about 60 minutes and includes heating, three-stage vacuum air extraction, sterilization and drying. Prior to autoclaving, the orthodontic archwires are packaged in a special foil for sterilization. The Runyes model B autoclave, model: Steam sterilizer SEA-12L-B, manufactured by Ningbo Runyes Medical Instrument Co., Ltd., HK, with three-stage vacuum airflow from the chamber and vacuum drying was used.

RESULTS

The transformation temperatures were determined by a thermal test (DSC). Table 1 lists the DSC results for the heating and cooling processes respectively, for CuNiTi archwires (as-received, as-received autoclaved and clinically retrieved) with a commercially A_f of 35° C. Also listed in the table is the duration of clinical usage for the clinically retrieved archwires, standard deviation heating onset temperature (A_s , M_s), finish temperature (A_f , M_f) and enthalpy for transformation in CuNiTi archwires tested. In Figure 1, the curves of the heating/cooling process can be observed. The results for the heating process show different A_f temperatures for all of the samples, but all of them do not go up to 35° C. The cooling curves for all samples were similar, with very small peaks. The A_f of the archwires before and after the clinical use varies insignificantly (~1° C).

Information about the presence or absence of the martensitic and austenitic phases is received by XRD analyses of the investigated orthodontic wires (Figure 2). The XRD analysis of the as-received, as-received autoclaved and used up to 6 and more than 8 weeks orthodontic archwires was made at room temperature. The diffraction patterns show typical peaks for Ni-Ti alloy with austenite structure. The austenitic phase has an ordered base-centered cubic structure, which occurs at high temperature. The as-received and as-received autoclaved samples show almost identical diffraction pattern with a maximum at 42.42° (austenite phase).

The SEM images (Fig. 3-6) of the surface topography revealed rough surface with many pores on all of the investigated CuNiTi archwires.

Table 1. DSC results for heating/cooling process of the investigated CuNiTi archwires

Wire	Wire	Heating process				
	Segment	Mass (mg)	As (°C)	Peak (°C)	Af (°C)	Enthalpy(J/g)
CuNiTi	As-received	5.045	9.80	20.60	28.00	10.9548
	As-received autoclaved	6.023	26.47	27.62	31.74	17.0411
	Up to 6 weeks	12.146	9.43	22.81	27.24	15.8621
	More than 8 weeks	4.115	12.91	21.79	27.02	8.2641
	Wire	Cooling process				
	Segment	Mass (mg)	Ms (°C)	Peak (°C)	Mf (°C)	Enthalpy(J/g)
	As-received	5.045	10.13	-1.10	-12.66	-12.6908
	As-received autoclaved	6.023	12.01	2.40	-4.76	-13.6155
	Up to 6 weeks	12.146	15.81	1.46	-7.67	-7.8784
	More than 8 weeks	4.115	10.71	-0.20	-11.42	-13.4704

Fig. 1. DSC heating/cooling curves for the investigated: a) as-received, b) as-received autoclaved, c) used up to 6 weeks and d) used more than 8 weeks CuNiTi archwires

Fig. 2. XRD patterns of the investigated CuNiTi archwires

Fig. 3. a) SEM micrograph (x 500) and b) EDX spectra of one area of as-received CuNiTi heat-activated orthodontic archwire

Fig. 4. a) SEM micrograph (x 500) and b) EDX spectra of one area of as-received autoclaved CuNiTi heat-activated orthodontic archwire

Fig. 5. a) SEM micrograph (x 500) and b) EDX spectra of one area of used up to 6 weeks CuNiTi heat-activated orthodontic archwire

Fig. 6. a) SEM micrograph (x 500) and b) EDX spectra of one area of used more than 8 weeks CuNiTi heat-activated orthodontic archwire

The EDX spectras (Fig. 3-6) and the averaged results for the elemental composition (Table 2) of all studied archwires are shown. The results show that there are only minimal variations in the chemical composition of the as-received, autoclaved and clinically retrieved CuNiTi archwires.

DISCUSSION

The clinical purpose of the new generation thermoactive archwires is to provide optimal force appropriate for the first stage of orthodontic treatment. Temperature transitions from martensite to austenite leads to reversible or irreversible changes in the alloys, which are expected to be useful for tooth movement. By these archwires the movement of the teeth is gradually accomplished within the biologically tolerable range. In this way, the patient's comfort is combined with sufficient force to move teeth or teeth segments into the desired position during the treatment. Orthodontic CuNiTi archwires (ORMCO Glendora, CA): as-received, as-received autoclaved and clinically retrieved from the same package, with variable advertised Af (35° C), were examined at the areas corresponding to premolars.

There are thermal studies of as-received CuNiTi ORMCO archwires that show Af ~32.2° C [6, 13]. Matthew et al [12] studies on as-received and clinically retrieved CuNiTi archwires showed differences within approximately ~2° C of the manufacturer's claim. Our DSC results revealed on as-received Af = 28° C and for as-received autoclaved 31.74° C. For the clinically retrieved Af is around ~27° C. The results are with temperature differences (~7° C) from what the manufacturer claimed. From this information it was assumed that the manufacturing differences amongst the variants is what caused the changes in Af. Joshua et al [6] observe presence of R phase upon heating and no R phase present upon cooling on as-received 35° C CuNiTi archwires. In our studies on the investigated archwires there is no presence of R phase upon heating and cooling.

The amount of force could be easily adjusted by the changes in the transition temperature range. For example, a thermoactive archwire with a transition temperature of 27° C placed in the patient's mouth releases heavier forces than an archwire with a transition temperature of 40° C. The first one turns to the austenitic phase in the mouth but the second is in martensitic phase because the transition temperature is not reached [1].

Due to the expressed interest of Bulgarian orthodontists, our research is conducted in order to improve the knowledge about the effect of autoclaving process on the archwires.

From the XRD analysis on the autoclaved archwire, a sharp peak can be observed, which indicates a better crystallite. Autoclaving process seems to have no effects on archwires' structure. After clinical usage there is an additional phase, which is probably formed on the surface of the archwires. Bigger pores are observed on the surface of the clinically retrieved orthodontic archwires due to the aggressive oral environment during treatment and masticatory function. Our results for the chemical composition of the as-received 35° C CuNiTi archwire from ORMCO show Cu 6.11 wt%, and for Ni and Ti: 47.07 wt% and 46.81 wt%, respectively, which differs from the results of Helge et al [14], whose study of the same wire shows that Cu weight percentage is 6.9 wt%, and for Ni and Ti are 50.7 wt% and 42.4 wt%, respectively. In other words, the archwire investigated by us contains less Ni. During the clinical use of the archwires in the patient's mouth, the elemental composition does not change significantly.

CONCLUSIONS

Commercially available 35 °C Thermo-active Copper NiTi archwires (as-received, as-received autoclaved and clinically retrieved) with rectangular cross-section were investigated. The DSC analysis of the studied 35° C CuNiTi archwires showed transition temperatures that differ with approximately ~7° C from the

Table 2. Elemental content of the investigated 35 °C CuNiTi archwires

Cu-Ni-Ti archwires	Elements, Weight %				
Spectrum	Ti	Ni	Cu	Error	Total
As-received	46.81	47.07	6.11	+/- 0.8%	100.00
As-received autoclaved	46.03	47.85	6.10	+/- 0.8%	100.00
Used up to 6 weeks	45.68	47.96	6.35	+/- 0.8%	100.00
Used more than 8 weeks	47.25	46.61	6.14	+/- 0.8%	100.00

commercially provided one. Also, no intermediate R phase was detected with the DSC. The XRD diffraction patterns show typical peaks for Ni-Ti alloy with austenite structure. The surface topography showed rough surface with scratches and porosities. The chemical content of the investigated as-received Cu-NiTi is Cu, Ni and Ti: 6.11 wt%, 47.07 wt% and 46.81 wt%, respectively. The autoclaving process has no influence on the chemical composition. Intraoral usage duration of the orthodontic archwires has no significant effect on the chemical content. The analysis confirms the presence only of the main elemental components of the alloy.

A good knowledge of the structural changes that occur in CuNiTi alloys in the oral cavity is useful for the orthodontists in order to optimize orthodontic treatment.

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