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Physicochemical characterization on clinically retrieved TriTanium orthodontic archwires

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The orthodontic archwire TriTanium® has three distinct thermally activated force regions which release the correct force in the anterior, premolar, and molar arch-regions in order to efficiently level, align and torque. During patient treatment, in the leveling phase of teeth alignment, fixed appliances in the frontal area require weak forces while for the lateral section greater forces are needed. This work aims to identify the chemical composition, structure and thermal behavior of clinically retrieved (at least six weeks wearing) TriTanium (0.41×0.56 mm^2) archwires. The studies were conducted in the three regions of elasticity: anterior – including the four incisions teeth, middle teeth – including the canine teeth and the premolars and the posterior e.g. the molars. To achieve the aim the following methods are used: XRD, EDX, SEM and DSC. The EDX analysis shows that Ni and Ti are the main elements in the composition of the examined archwires and the 1:1 ratio of elements is kept during treatment. The room temperature XRD patterns show typical peaks for a Ni-Ti alloy with austenite type structure. SEM micrographs show different morphology in the three (3) zones of the investigated archwires. The DSC measurements were conducted in the –50 °C to +50 °C temperature range and revealed three phase transitions (austenite, martensite and R-phase) in the 3 zones. The wearing of the archwires in the patients' mouth alters the thermal phase transitions in the three investigated regions of TriTanium archwires.

Keywords: clinically retrieved TriTanium archwire, XRD, SEM, EDX, DSC.

INTRODUCTION

The variety of materials used in orthodontics is considerable. As elements orthodontic archwires are of great importance for the teeth correction treatment mainly using the fixed orthodontic technique. They are as well the main source of force in orthodontic treatment [1].

Over the years biomaterials have improved in orthodontics to allow orthodontists to get closer to the ideal of weak incessant forces to achieve rapid tooth movement without damaging teeth or periodontal tissues [2]. The shape of the archwires has also evolved from round, square and rectangular to bevelled surfaces [3]. The ideal orthodontic archwire would provide relatively weak biomechanical force and wide elastic (working) range for tooth movement. It needs to be easily manipulated to avoid fracture and to be "joined" to form more complex appliances. It should not present concerns regarding *in-vivo* corrosion and problematic ion release and finally should be relatively inexpensive. None of the metallic orthodontic wires meet all of these desired aspects fully, and rational clinical selection involves consideration of a balanced performance for any particular case [1].

There are many types of orthodontic archwires depending on the metal alloy used. Nowadays, one of the most used is the NiTi type of archwires. They have the property of exerting permanent weak forces,

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appropriate for alignment and leveling, therefore NiTi archwires are used in the early stages of orthodontic treatment [4, 5].

There are few types of NiTi archwires- martensite-stabilized, martensite-active and austenite-active [5]. In the last few years new archwires with 3 zones of elasticity "TriTanium" have been introduced on the market. At first, due to its high porosity and good acceptance by human body, the TriTanium (Ni-Ti) alloy has been used in orthopedics [6]. In orthodontics, this alloy is valuable, because of its three zones of elasticity in the anterior, mid-region and posterior segments. The root systems of the teeth in those 3 segments are quite different, due to this an archwire that can apply forces suitable for each zone is considered to be more effective, especially in the initial phase of fixed appliance treatment. It is believed that patient comfort improves, due to the minimization of the incidence of root resorption by the multi-force orthodontic archwires [7, 8].

Up to this moment there are only studies about as-received TriTanium archwires [7, 9]. The purpose of this study was to investigate and compare the differences between as-received and clinically retrieved TriTanium archwires, after several weeks of use in patients' mouth and to complete information on their physicochemical properties and behavior during treatment. Revealing this information is an important condition for the proper choice of an archwire for a certain stage of the orthodontic treatment.

EXPERIMENTAL

Six cut pieces of clinically retrieved (up to 6 weeks and more than 8 weeks) TriTanium orthodontic archwires with dimension 0.41×0.56 mm^2 (0.016"×0.022"), produced from American Orthodontics were investigated. The same pieces of the TriTanium archwire were cut from the areas corresponding to the anterior, premolar and molar segments. The tests were performed with techniques: XRD, SEM, EDX and DSC for characterizing the surface microstructure, chemical composition and thermal phase transition on investigated TriTanium orthodontic archwires.

The crystalline structure was assessed by powder diffraction, on a D8-Advance, Bruker powder diffractometer with a Cu-Kα target, within the range from 5–80° 2θ at a constant step 0.02° 2θ. The SEM images of the samples were obtained by means of FEI Nova NanoSEM 230 microscope, equipped with Schottky field emission gun. The compositions of the samples were determined using EDX (Energy Dispersive X-ray Spectroscopy) method with Bruker Esprit 1.8 system. The accelerating voltage for the EDX measurements was 20 kV. Quantification of the EDX results was performed by the help of PB-ZAF standardless method. The Differential scanning calorimetry (DSC) analyses were performed using a DSC Perkin-Elmer – 8000. Before introducing the sample in the DSC apparatus for each individual test a calibration with indium was made. The temperature range of the DSC apparatus is from –170 °C to +600 °C. The samples were scanned from –50 °C to +50 °C for the heating process and from +50 °C to –50 °C for the cooling process, with a temperature gradient of 10 °C per minute. The onset and endset temperature along with enthalpy of all investigated archwires were calculated for various phase transformations.

RESULTS AND DISCUSSION

In our previous studies we have shown that the as-received TriTanium archwires in three regions besides the austenite crystal structure show a small degree of amorphization of the material seen on XRD spectra [9]. In the clinically retrieved TriTanium archwires the austenite structure is kept in the three regions during treatment, shown by XRD spectra made at room temperature (Fig. 1). This behavior is also seen in the Cu-Ni-Ti and Ni-Ti heat-activated archwires [4, 10] and can be due to contamination.

The elemental content of investigated archwires with EDX analysis is presented in Table 1. The analysis is made to determinate the main components in the TriTanium alloy in the three regions. The EDX results revealed that Ni and Ti are main components along the archwire. The period of residence in the mouth has no significant effect on the proportion

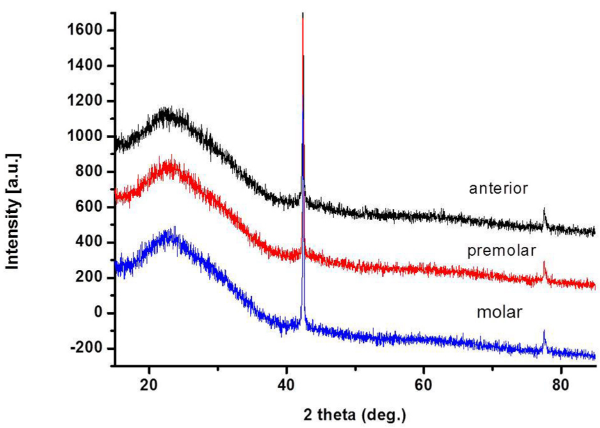

Fig. 1. X-Ray diffraction patterns on investigated Tritanium archwires.

Table 1. Element content on investigated Tritanium archwires

Segment	As-received		Up to 6 weeks		More than 8 weeks		Error [%]
wt%	Ti	Ni	Ti	Ni	Ti	Ni	± 0.8%
Anterior	50,55	49,45	50,40	49,60	50,77	49,23	± 0.8%
Premolar	50,73	49,45	51,52	48,48	50,22	49,78	± 0.8%
Molar	50,73	49,27	51,72	48,28	50,10	49,90	± 0.8%

of elements in the tested orthodontic archwires and the ratio Ni to Ti is kept. The average value of the clinically retrieved TriTanium archwires is Ni 51.21 wt% and Ti 48.79wt% for used archwire up to 6 weeks and Ni 50.36 wt%. and Ti 49.64wt% for archwire used more than 8 weeks.

The surface morphology of an orthodontic wire is an essential functional property known to influence the mechanical characteristics, the corrosion behavior, and/or the biocompatibility of wires. The resulting surface structure depends on the alloy used, the complex manufacturing processes, and the surface finish treatment [11, 12].

From SEM micrographs (200 µm) made on the surface of clinically retrieved archwires such surface defects and scratches were visible on all (anterior, premolar, molar) regions, and were comparable with the irregular surface of as-received archwires [9] (Fig. 2a, Fig. 2b). These defects and scratches can be related to an occasional mechanical impact during manufacturing, for example manipulating during cutting or holding with instruments [13]. The scratches may be result of bracket–archwire contact areas. Increase of surface defects on the clinically retrieved archwires is resulting from manipulations during orthodontic treatment.

Plaque and food remnants were found on all investigated samples (Fig. 2). Figure 3 shows the results from the SEM-EDX analyses of the TriTanium sample in anterior region used up to 6 weeks. The analyses showed the presence of organic and inorganic compounds.

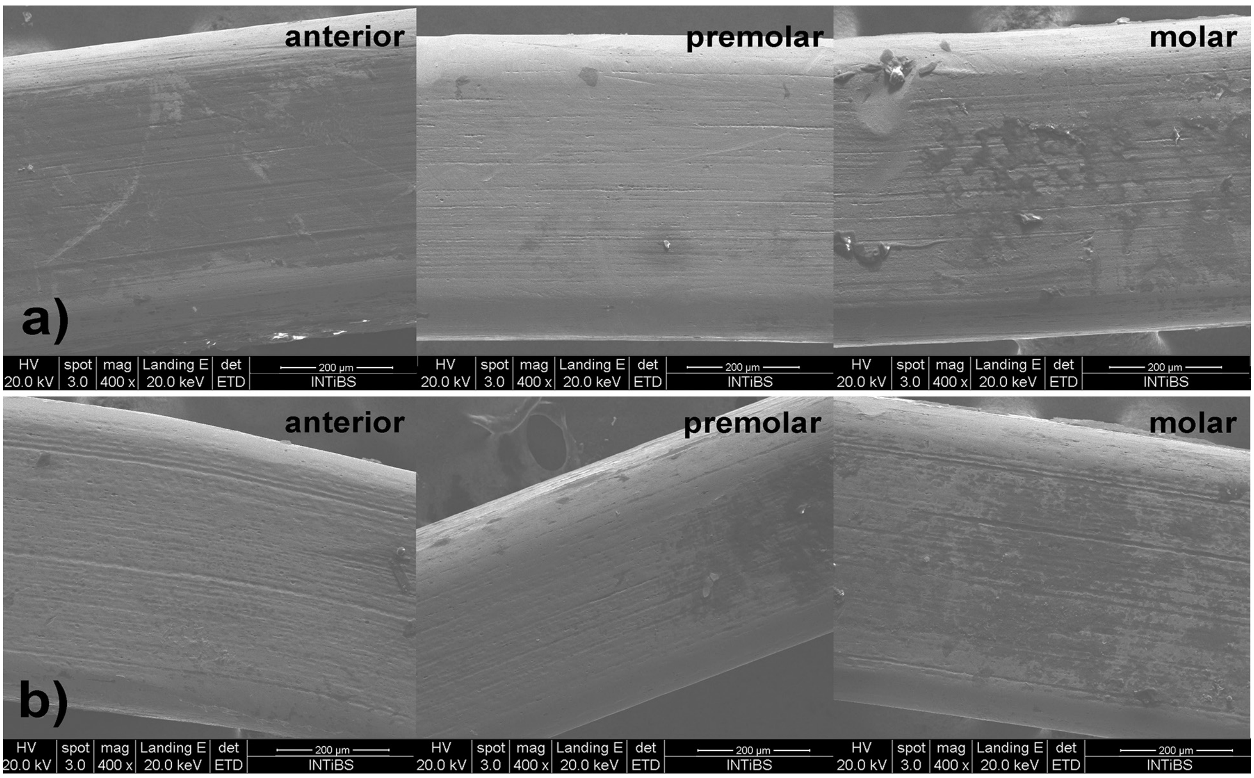

Fig. 2. SEM micrographs of the surface of the investigated TriTanium archwires: *a*) used up to 6 weeks, *b*) used more than 8 weeks.

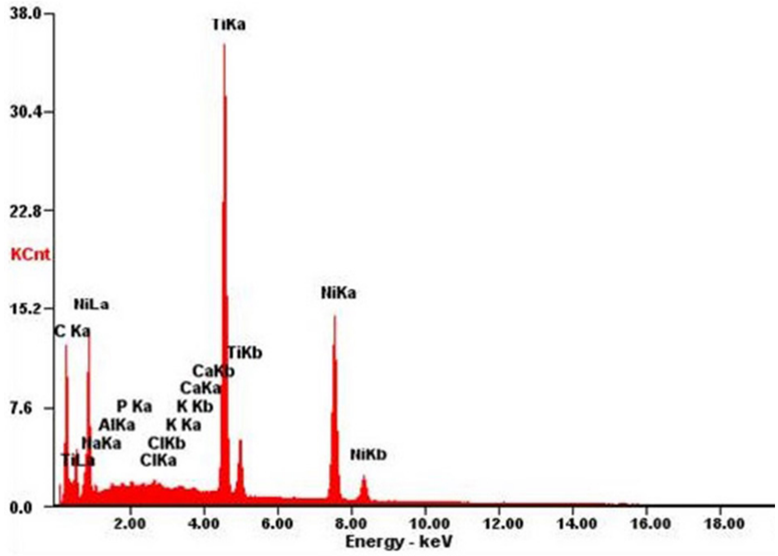

Fig. 3. EDX analyses on clinically retrieved up to 6 weeks Tritanium archwire (anterior region).

As it is well-known the TriTanium alloy is highly porous [14] and as seen on the SEM micrographs made on the surface of the investigated archwires one cannot observe any grains or pores. Thus we made a SEM analyses on a cross section on each sample (Fig. 4). Before placing the polished sample in the FEI Nova NanoSEM 230 microscope we covered them with nitric acid on the cross section surface, waited few minutes and after that we cleaned the sample with distilled water. Treatment with the acid can remove the accumulation of impurities such as N, P, Ca, K, Al, Si, Fe, from the surface of TriTanium archwires. Secondly, it improves the surface chemistry and also increases the surface area by opening the mouth of the pore [15]. On Figure 4 are SEM micrographs (200µm) on clinically retrieved TriTanium archwires. It can be seen that the clinically retrieved more than 8 weeks archwires (Fig. 4b) have higher porosity than the clinically retrieved up to 6 weeks ones (Fig. 4a).

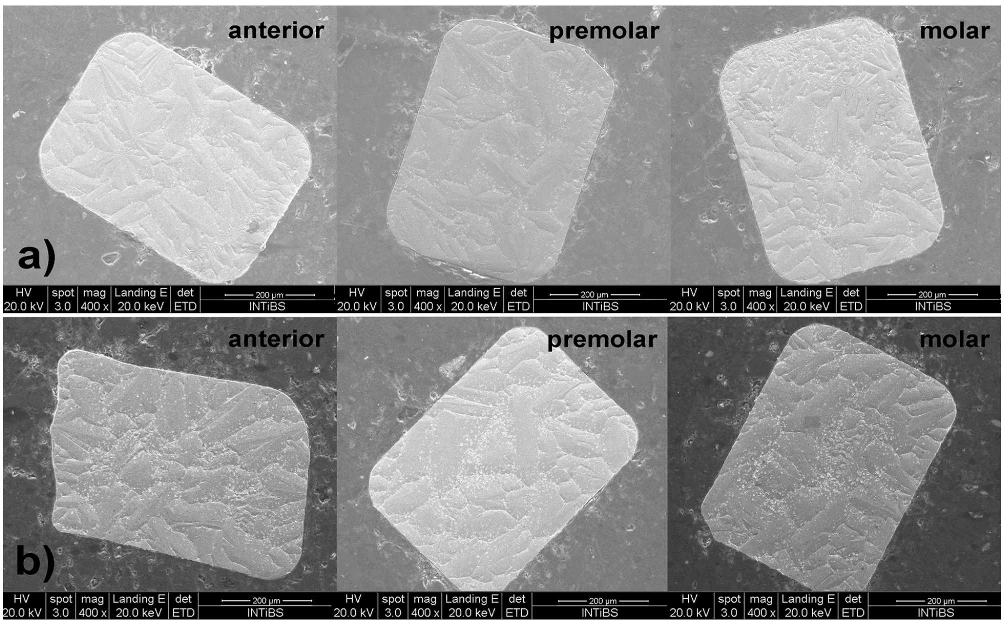

Fig. 4. SEM micrographs on cross section on investigated the TriTanium archwires: *a*) used up to 6 weeks, *b*) used more than 8 weeks.

XRD studies made at room temperature show that the three regions of the clinically retrieved TriTanium archwires possess an austenite structure. To trace the thermal behavior of the clinically retrieved archwires and the austenite/martensite transition we carried out DSC analyses in the temperature range –50 °C to +50 °C. We choose to investigate the archwires in the interval from –50 °C to +50 °C, because we expect the archwire to be "completely" in martensite state at –50 °C. In clinical environment the orthodontist can cool the surface of the archwire to lower temperatures with spray. The upper temperature +50 °C is higher and close to the maximum temperature in the oral cavity [16] and the alloy is completely transformed in austenite state. The austenite phase/formation in a cyclic process was verified by DSC analysis of the clinically retrieved TriTanium orthodontic wire. For this, a sample of rectangular orthodontic wire underwent two cyclic processes as follows: the sample was heated up to 50 °C at a rate of 10 °C min^{-1}. Then, the sample was cooled, also at a rate of 10 °C min^{-1}, to –50 °C. Afterward, all the heating–cooling steps were repeated.

In Table 2 and Table 3 the DSC and temperature curves are recorded for clinically retrieved TriTanium archwires (up to 6 weeks and more than 8 weeks), for the two cycles in their three region as follows: anterior, premolar and molar. In both cycles, on the DSC curve for investigated archwire (up to 6 weeks of clinical usage), the thermal effects of austenitic phase transitions for anterior As = 17.93 °C and Af = 27.97 °C, premolar As = 22.54 °C and Af = 26.78 °C and molar As = 14.57 °C and Af= 24.30 °C were identified. The same identification was done for investigated archwire (more than 8 weeks of clinical usage): anterior As = 21.03 °C and Af = 25.22 °C, premolar As = 16.87 °C and Af = 33.59 °C and molar As = 17.56 °C

Table 2. DSC curves on investigated Tritanium archwires – heating process

Tritanium archwire	Wire segment	Heating process		Wire segment	Heating process		Wire segment	Heating process	
		As temp (°C)	Af temp (°C)		As temp (°C)	Af temp (°C)		As temp (°C)	Af temp (°C)
Literature*	Anterior	18.2	**25.5**	Premolar	17.0	**24.4**	Molar	11.8	**20.5**
As-received**		16.16	**25.55**		11.92	**21.23**		8.26	**20.82**
Up to 6 weeks		17.93	**27.97**		22.54	**26.76**		14.57	**24.30**
More than 8 weeks		21.03	**25.22**		16.87	**33.59**		17.56	**23.53**

Table 3. DSC curves on investigated Tritanium archwires – cooling process

Tritanium archwire	Wire segment	Cooling process			
		Rs temp (°C)	Rf temp (°C)	Ms temp (°C)	Mf temp (°C)
Literature*	Anterior	16.2	11.5	–22.5	–34.5
As- received**		12.99	6.93	–21.07	–36.80
Up to 6 weeks		17.16	9.91	–19.76	–35.02
More than 8 weeks		–	–	22.56	13.04
Literature*	Premolar	16.5	13.0	–25.5	–39.5
As- received**		12.76	6.57	–30.93	–46.17
Up to 6 weeks		14.35	9.96	–21.92	–36.40
More than 8 weeks		–	–	22.16	15.94
Literature*	Molar	14.6	9.4	–33.3	–48.5
As- received**		12.28	3.17	–38.95	–35.11
Up to 6 weeks		–	–	15.64	9.40
More than 8 weeks		–	–	24.15	13.08

* Thermomechanical characterization of variable force NiTi orthodontic archwires, Anjali Sudershan Krishan Mehta, Marquette University.

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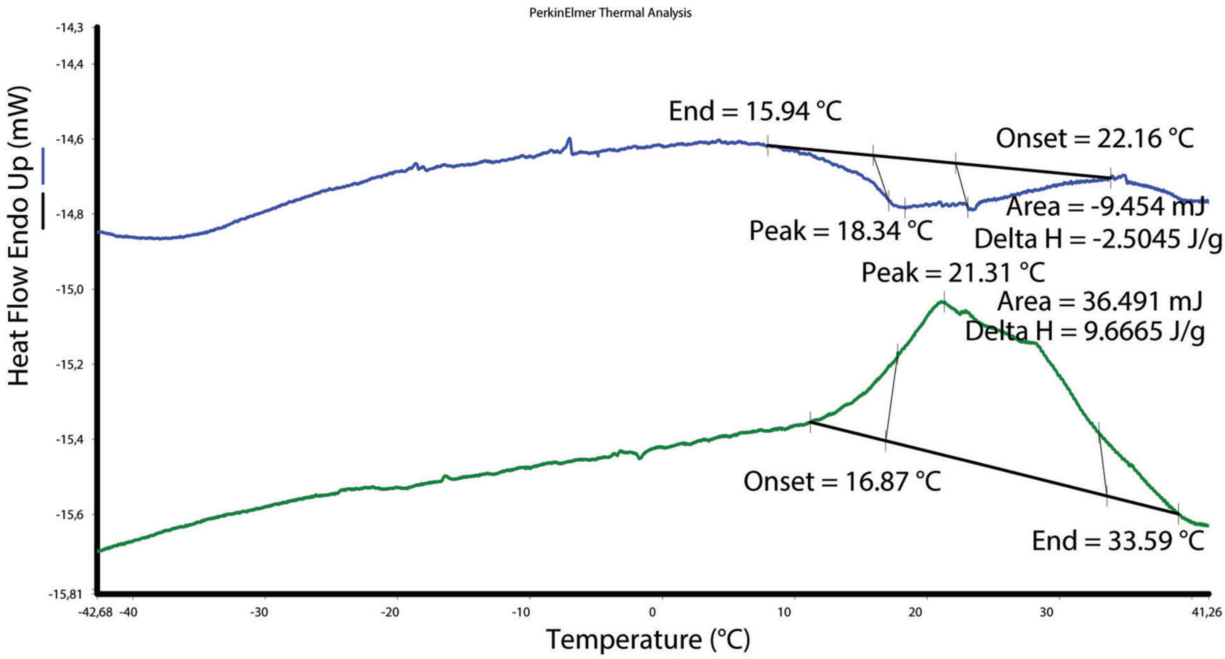

Fig. 5. DSC curves heating/cooling for Tritanium archwire used for more than 8 weeks (premolar region).

and Af = 23.53 °C. Other studies for as-received TriTanium archwires have Af = 25.5 °C for anterior, Af = 24.4 °C, Af = 21.23 °C for premolar and Af = 20.5 °C, Af = 20.82 °C for molar region (Table 2) [7, 9]. Compared to other studies we noticed an increase of Af in clinically retrieved archwires, especially in premolar region in clinically used more than 8 weeks (Fig. 5). Values of the martensitic formation was also obtained for both archwires, with a maximum of Ms = –21.92 °C and Mf = –36.40 °C for investigated archwire up to 6 weeks clinical usage in premolar region. Differential scanning calorimetric studies have identified the presence of additional peaks during the heating/cooling curves, and they have been attributed to the presence of an intermediate rhombohedral "R" phase. This phase may be present in some proportion relative to the other two phases [7]. The studies of as-received TriTanium archwires show presence of R-phase in the three regions [9]. The investigated clinically retrieved TriTanium archwires have R-phase only in anterior and premolar regions of clinical usage up to 6 weeks.

Based on the obtained results, we show austenitic, martensitic and R-phase phases with different thermal transition temperatures amongst the as-received and clinically retrieved TriTanium archwires. As the time of clinical usage is increasing it can be noticed a temperature difference especially for Af temperature in the premolar region. We assume that the changes in the canine teeth region (premolar) might be due to their placement in the most curved part of the archwire and in that region the tensions are the greatest [17]. This is the most exploited and "amortized" part of the archwire. The investigated TriTanium archwire do in fact deliver different forces depending on the region (anterior, premolar, molar). The manufacturing steps and also the duration of the archwires in the patients' mouth can alter their thermal transitions.

CONCLUSIONS

This study contributes to the establishment of some peculiarities related to the thermal behavior of the investigated archwires. Our studies revealed that after a prolonged period of time in the patient's mouth, the investigated regions of TriTanium archwire have no significant changes in the elements ratio close to 1:1 (Ni 51.21 wt% and Ti 48.79wt%) for archwire used up to 6 weeks and Ni 50.36 wt%. and Ti 49.64wt% for archwire used more than 8 weeks. From SEM analyses made on the surface of clinically retrieved archwires surface defects and scratches were visible in all regions. On the SEM micrographs made on the cross section the porosity of the TriTanium alloy is observed. The clinically retrieved more than 8 weeks archwires have higher porosity than the clinically retrieved up to 6 weeks ones. From XRD analyses we observed that clinically retrieved TriTanium archwires have austenite structure at room temperature in the three regions during treatment. Based on the results obtained by DSC, we show different thermal transition temperature of austenitic, martensitic and R phase phases amongst the as-received and clinically retrieved TriTanium archwires. As the time of clinical usage is increasing it can be noticed a temperature difference especially Af temperature in the premolar region with ~8°C. The duration of the archwires in the patients' mouth alters the thermal phase transitions in the three investigated regions of TriTanium archwires.

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