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Structural and morphological characterization of heat-activated nickel-titanium archwires

I. Ilievska[1]*, V. Petrov[2], L. Andreeva[2], D. Kovacheva[3], A. Zaleski[4], M. Drozd[4], E. Bukowska[4], V. Mikli[5], A. Stoyanova-Ivanova[1]

[1] *Institute of Solid State Physics, BAS, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia,Bulgaria*
[2] *Faculty of Dental Medicine, Medical University Sofia,St. Georgi Sofiiski Blvd., 1431 Sofia, Bulgaria*
[3] *Institute of General and Inorganic Chemistry, 1113 Sofia „Acad. Georgi Bonchev" str. bld.11*
[4] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okolna 2, 50-422 Wroclaw, Poland*
[5] *Centre for Materials Research, Tallinn University of Technology, Ehitajate 5, Tallinn 19086, Estonia*

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Heat-activated nickel-titanium (Ni-Ti) archwires are widely used in the initial stages of orthodontic treatment. These alloys exhibit a shape memory effect which can be related to displacive (martensitic) transformation, which can be induced by temperature variation or mechanical influence (stress).

Here we explored the changes of archwires microstructure, chemical composition and phase transition temperatures due to prolonged regular usage. Three forms of dental archwires with dimensions 0.016" x 0.022" (3M Unitek, Monrovia, CA, USA) were investigated: as-received, as-received + autoclaved (sterilized) and used during treatment heat-activated Ni-Ti archwires. The three forms of archwires were analyzed by powder X-ray diffraction analysis (XRD), Scanning Electronic Microscopy (SEM) in combination with Energy Dispersive Spectroscopy (EDX) and Differential Scanning Calorimetry (DSC).

The room temperature the XRD pattern of the archwires show typical peaks for a Ni-Ti alloy with austenite type structure. The DSC measurements were conducted in the –50°C to +50°C temperature range. The DSC analyses of the Ni-Ti archwires revealed three phase transitions. Upon heating from –50°C to +50°C a phase transition occurs at ~12°C. No additional *endo*/*exo* effects are registered. Upon cooling the DSC registers a phase transition around 10°C and around –40°C. The first effect is due to the formation of an intermediate rhombohedral phase (R phase) while at –40°C Ni-Ti structure transforms to martensite. The results from EDX demonstrate that there is no pronounced change in the chemical composition on the surface of the investigated orthodontic archwires. Though SEM micrographs show some changes on the surface of the wires after usual use.

The results obtained within this study contribute to the establishment of some peculiarities related to the thermal behavior and the shape-memory effect of the investigated archwires.

Keywords: Ni-Ti heat-activated orthodontic archwires, XRD, SEM, DSC.

INTRODUCTION

Nickel-titanium (Ni-Ti) archwires are used in the initial stages of orthodontic treatment due to their properties of exerting light constant forces that are appropriate for alignment and leveling and good super-elasticity. [1–3]

An interesting feature of these heat-activated archwires is their thermoelastic behavior and the so-called shape memory effect, which has remarkable clinical applications. During bending and repeated temperature cycles, orthodontic archwires in the austenitic phase are able to „remember" a pre-formed shape, including specific shape of the dental arch [4]. The Ni-Ti archwires transform from martensitic to austenitic phase at oral temperature (35 degrees). At lower temperatures the martensitic phase is fully present in the alloy, which allows the orthodontist to easily put the orthodontic arch into the slot of the bracket. At higher temperatures the alloy turns to the austenite phase and starts exerting larger forces, due to the return to its original shape. These forces make teeth move in a certain direction [5, 6].

* To whom all correspondence should be sent:
E-mail: ivannyilievska@gmail.com

During orthodontic treatment, Ni-Ti archwires in the patient's mouth are exposed to frequent temperature changes, which are more complex than those observed in the in - vitro studies [7]. Accordingly, the orthodontic archwires will be subjected to loads, complex temperature fluctuations, as well as interaction with the brackets, which are with different metal composition. The wires can also interact with electrolytes, fluoride, proteins, etc., and that leads to formation of new compounds on the surface. The combination of these factors could affect the properties and structure of archwires, although there is little information in the literature about the effects of these factors on clinically used orthodontic archwires [8].

In our previous studies we examine the chemical composition of the surface of thermally activated copper-nikel-titanium archwires [9].

In this study we concentrate not only on investigating the chemical composition and the structure, but also on investigating the thermal phase transition on as-received, as-received autoclaved (sterilized) and used heat-activated Ni-Ti archwires, because their action is influenced by temperature. The process of autoclaving (sterilization) has also been studied. The results obtained within this study contribute to the establishment of some peculiarities of the thermal behavior and the shape-memory effect of the archwires.

MATERIALS AND METHODS

Three types of dental orthodontic archwires with a rectangular cross section and dimensions 0.016" × 0.022" (0.406 mm × 0.558 mm) were chosen: as-received, as-received autoclaved (sterilized) and used (up to 5 and 8 weeks) heat-activated Ni-Ti archwires, produced by the company 3M Unitek, Monrovia, CA, USA. The analyses were carried out by the following techniques: X-ray diffraction analysis (XRD), Scanning Electronic Microscopy (SEM), Energy Dispersive Spectroscopy (EDX) and Differential Scanning Calorimetry (DSC).

To determine the structure of the material we use an X-ray Powder Diffractometer X'Pert Pro with a high-temperature closed attachment HTK 1200 from Anton Paar.

Surface morphology and elemental composition were studied using a ZEISS HR FESEM Ultra 55 Scanning Electron Microscope (SEM) with Bruker EDX system ESPRIT 1.8. The elemental composition was determined by energy-dispersive X-ray microanalysis (EDX) method using Bruker Esprit 1.8 system. Quantification of the EDX results was performed by the help of interactive PB-ZAF standardless method. The acceleration voltage for SEM measurements was 4.0 kV and for EDX 7.0 kV.

The analyses by Differential Scanning Calorimetry (DSC) were performed using a DSC Perkin-Elmer – 8000 with TGA attachment, model PE-TGA4000. 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 heating/cooling rate of 20°C per minute. The onset and endset temperatures along with enthalpy of all investigated archwires were calculated for various phase transformations.

RESULTS AND DISCUSSIONS

Information about the presence or absence of the martensitic and austenitic phases is received by XRD analyses of the Ni-Ti heat-activated orthodontic wires [10]. On Fig. 1, the XRD pattern made at room temperature on as-received, as-received sterilized and used up to 5 and up to 8 weeks orthodontic archwires, we observed typical peaks for Ni-Ti alloy with austenite type structure. The austenitic phase has an ordered base-centered cubic structure, which occurs at high temperature [11]. It can be seen that there is a presence of a surface amorphization of the material, which can be due to surficial interaction with saliva or contamination. Similar behavior is seen in the Cu-Ni-Ti heat-activated archwires [9].

Information about the surface morphology of the Ni-Ti heat-activated orthodontic archwires is obtained by Scanning Electron Microscopy (Fig. 2.)

The results demonstrate that there is no remarkable change on the surface of as-received and as-

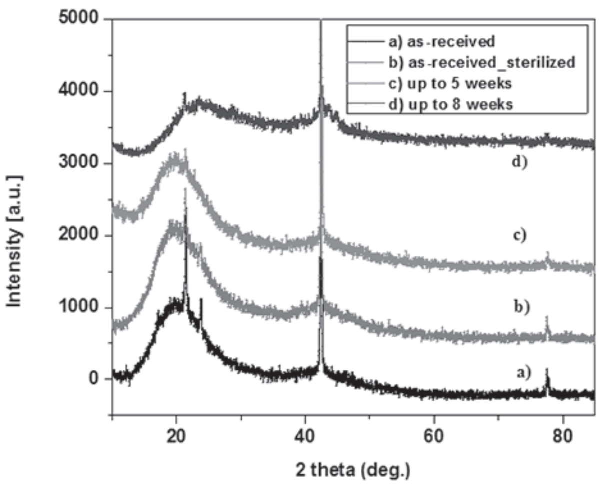

Fig. 1. XRD pattern of investigated Ni-Ti archwires at different stages of treatment.

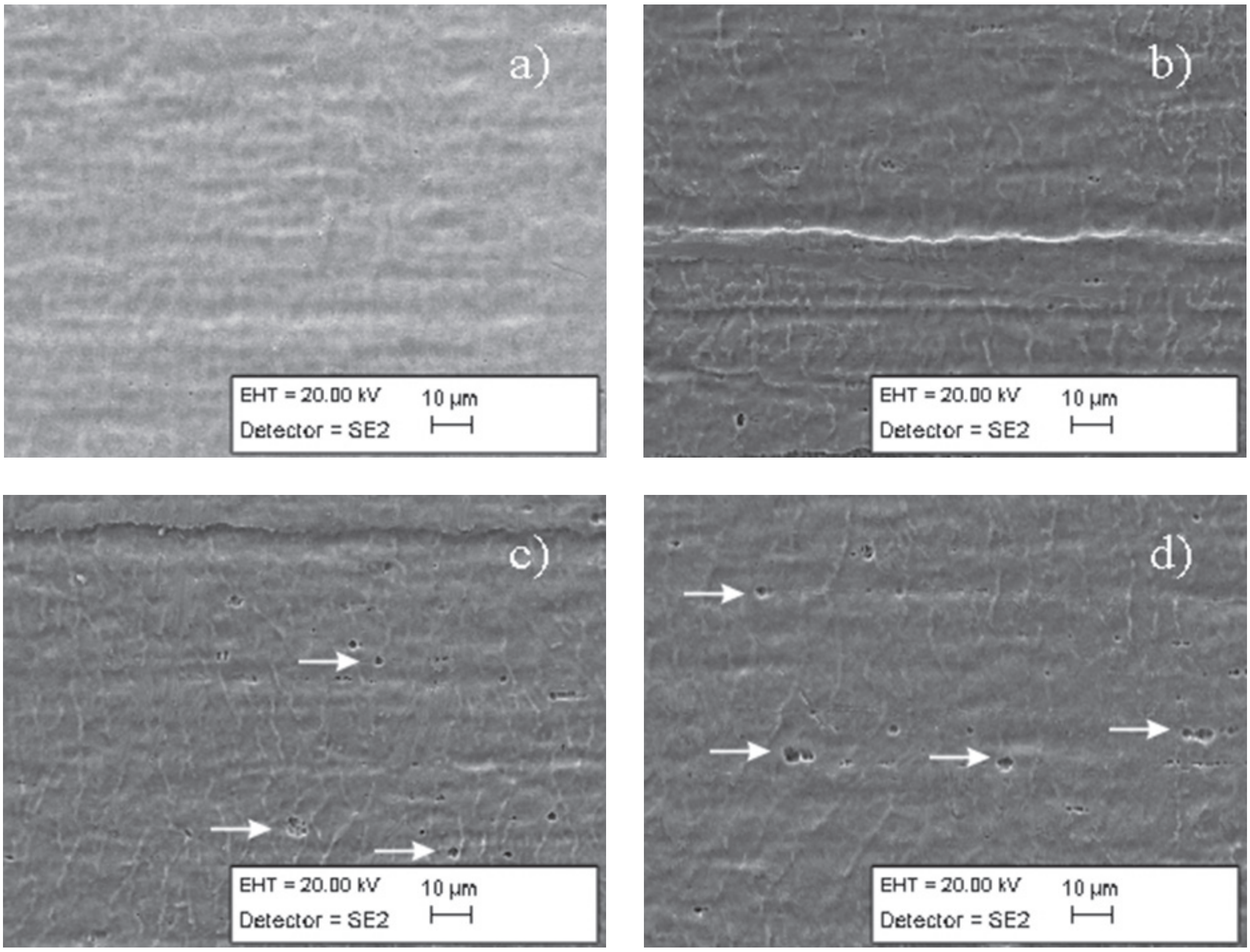

Fig. 2. SEM images of as-received a), as-received sterilized b), used up to 5 weeks c), used up to 8 weeks d) Ni-Ti heat-activated orthodontic archwires.

received sterilized archwires. Autoclaving process seems to have no effects on archwires' structure. On the surface of the archwires that have been used for treatment up to 5 and up to 8 weeks it can be seen that there is a change after use. The presence of the bigger pores can be observed on the surface of the used archwires, which can be the result of an aggressive environment in the mouth during treatment and masticatory action.

Also the EDX was used to analyze the surface of the archwires and to make quantitative identification of the chemical composition by elements. The average values of the element composition are shown in Table 1.

The results show that as-received Ni-Ti heat-activated archwire has average Ni – 54.36 wt% and Ti – 45.64 wt%. The period of residence in the mouth has no significant effect on the proportion of elements in the tested orthodontic archwires and the ratio Ni to Ti is kept. The analysis confirms the presence of only the main components of the alloy.

Ni-Ti archwires are heat-activated orthodontic archwires with shape-memory properties. Phase transformations (austenite – martensite) in these archwires are of big importance due to their clinical applications. That's why we chose the DSC method for investigating phase transformations and because this method provides information about the entire sample [12].

DSC can give information about the thermal transitions of the material, in our case we measured our samples in the temperature range from –50°C to +50°C and back to –50°C with heating/cooling of 20°C per minute to see the transformation temperatures and associated transformation enthalpy changes, respectively. The transition temperature range (TTR) in Ni-Ti alloys, which happens when phase transition occurs, should correspond to the temperature variations in the oral environment to be beneficial for the orthodontic treatment [13]. Information about TTR for rectangular Ni-Ti archwires with dimensions 0.016" × 0.022", are in need because

Table 1. Elements content of investigated Ni-Ti archwires

Ni-Ti archwires	Elements, weight %				
Spectrum	Ni	Error	Ti	Error	Total Ni-Ti
Ni-Ti as-received	54.36	+/– 0.8%	45.64	+/– 0.8%	100.00
Ni-Ti as-received sterilized	54.41	+/– 0.8%	45.59	+/– 0.8%	100.00
Ni-Ti up to 5 weeks	54.13	+/– 0.8%	45.87	+/– 0.8%	100.00
Ni-Ti up to 8 weeks	54.19	+/– 0.8%	45.81	+/– 0.8%	100.00

there is no enough studies about it. The manufacturers do not provide complete information about the produced archwires as well.

The transformation from austenite to R-phase and from R-phase to martensite has been investigated by DSC method [14], where As (austenite start), Rs (R-phase start) and Ms (martensite start) are the onset temperatures when the transition begins. Respectively, Af (austenite finish), Rf (R-phase finish) and Mf (martensite finish) are the endset temperatures when the transition ends.

Table 2 and table 3 show our results obtained by DSC: transformation temperatures (onset, endset), enthalpy of the transition (ΔH), the peak and the area under the curve, which were measured for all investigated archwires. An intermediate tetragonal phase between austenite and martensite called R-phase can occur as a result of a rhombohedral distortion of the cubic parent phase [10] and the lower temperature phase is rhombohedral. The R-phase transition is a kind of martensitic transformation with a very small thermal hysteresis [15]. In our case, we observed the intermediate R-phase in the cooling process.

In as-received Ni-Ti archwire, from the DSC analyses made in the temperature range from –50°C

Table 2. DSC results for heating process of the investigated archwires

Ni-Ti heat-activated archwires	Heating				
	Onset [°C]	Delta H [J/g]	Peak [°C]	Area [mJ]	Endset [°C]
	As				Af
As-received	4.35	6.3539	10.91	79.048	17.57
As-received sterilized	6.97	7.8037	10.93	33.056	13.86
Used up to 5 weeks	12.90	10.0995	18.20	37.934	21.34
Used up to 8 weeks	6.21	9.3893	11.43	49.979	15.52

Table 3. DSC results for cooling process of the investigated archwires

Ni-Ti heat-activated archwires	Cooling									
	Onset [°C]	Delta H [J/g]	Peak [°C]	Area [mJ]	Endset [°C]	Onset [°C]	Delta H [J/g]	Peak [°C]	Area [mJ]	Endset [°C]
	Rs				Rf	Ms				Mf
As-received	11.93	–2.1860	3.01	–27.19	–3.16	–	–	–	–	–
As-received sterilized	24.19	–2.9258	3.46	–12.394	–1.38	–42.59	–0.8540	–46.62	–3.618	–49.34
Used up to 5 weeks	24.89	–3.5700	11.28	–13.409	3.94	–35.91	–4.7536	–41.66	–17.85	–47.19
Used up to 8 weeks	9.03	–2.9202	3.40	–15.544	–2.61	–42.78	–0.7760	–47.08	–4.131	–49.74

to +50°C and back to –50°C, it can be observed that there is a transition from austenite to R-phase, without the presence of martensite phase (Fig. 3a). For the as-received sterilized Ni-Ti archwire, in the cooling process there are two peaks which are attributed to an austenite to R-phase followed by an R-phase to martensite transition. (Fig. 3b). The Af in the heating process for as-received and used archwires, is changing during treatment from 17.57°C to 15.52°C. The Af is particularly important, since it indicates the temperature in which the material will entirely return to the original shape and consequently acquire greater rigidity [13].

Brantley et al. reported that the R-phase may always be present in some Ni-Ti heat-activted archwires [16]. DSC analyses of investigated as-received Ni-Ti archwire do not show presence of martensite phase in the measured temperature interval.

On Figure 4 results from DSC for the used archwires (up to 5 weeks (a) and up to 8 weeks (b)) are shown. The presence of the R-phase is observed in the cooling process for the used archwires as well. The Ms temperature for as-received sterilized and used archwires is below –30°C. It can be seen that every phase transition has different transition temperatures for investigated archwires. Other studies of orthodontic archwires produced form other companies used for the same purpose show differences from our results [1]. This requires prolonged study of applied orthodontic archwires in each step of treatment.

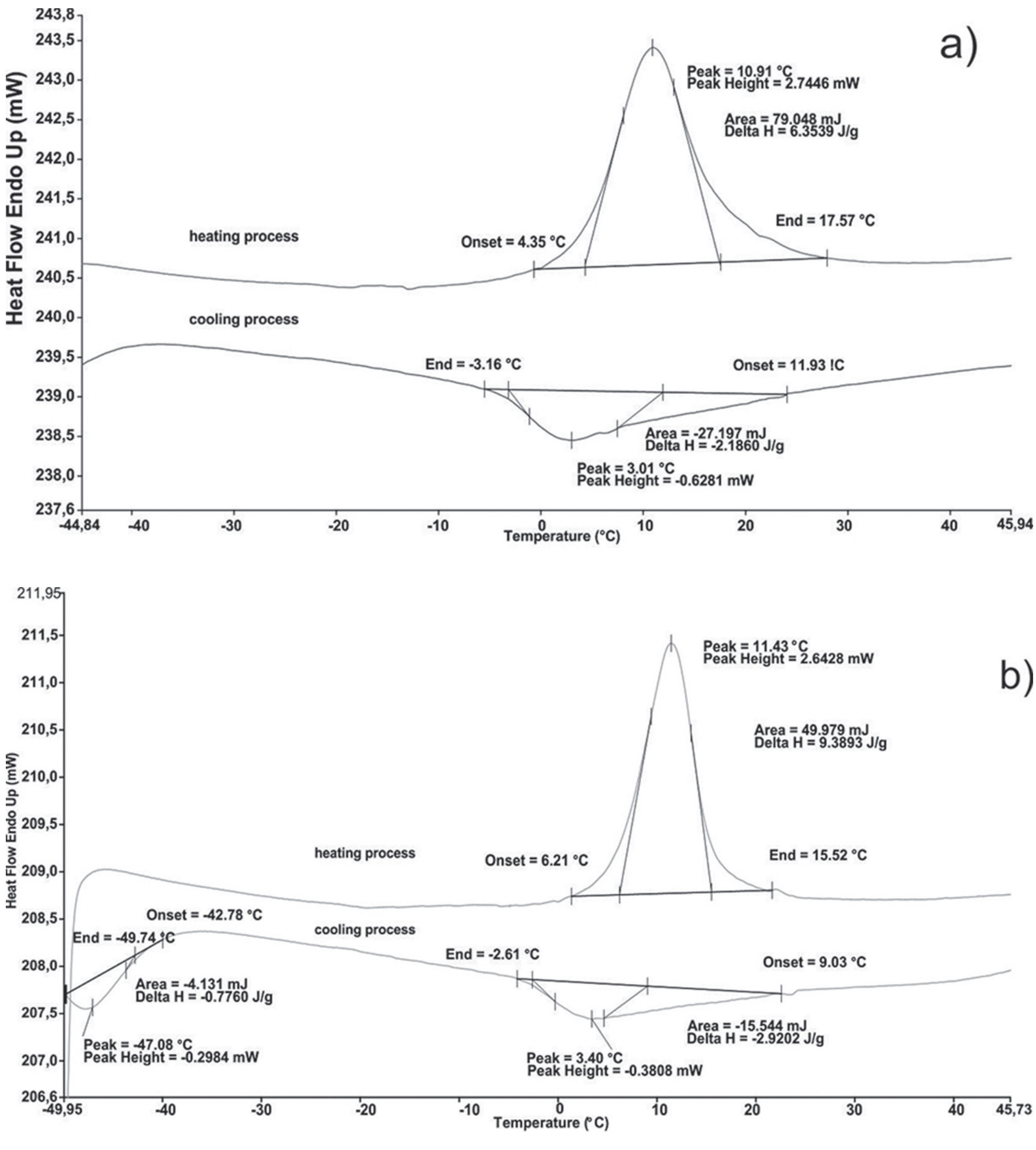

Fig. 3. DSC analyses on as-received a) and as-received sterilized b) Ni-Ti archwires.

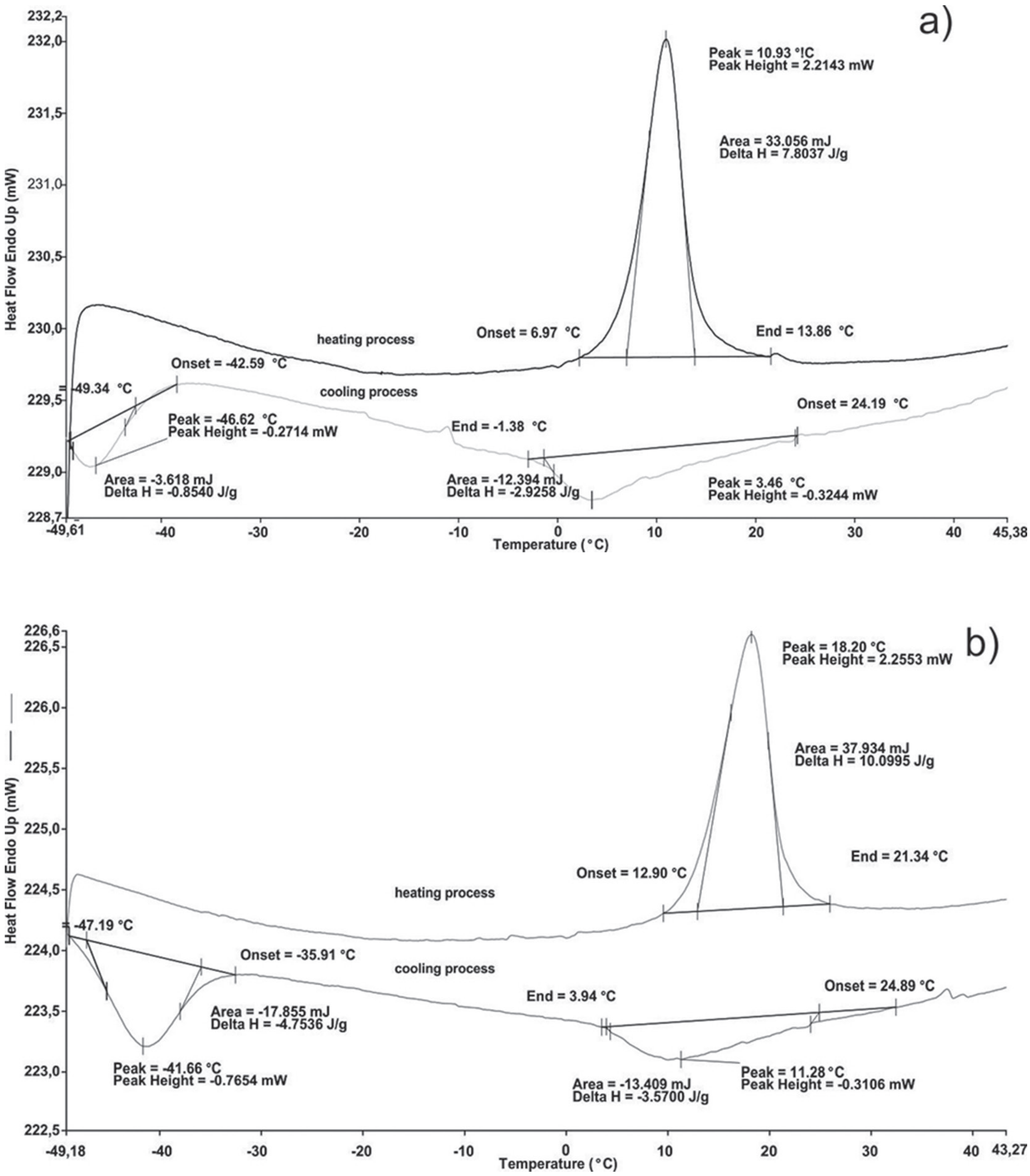

Fig. 4. DSC analyses on Ni-Ti archwires used up to 5 weeks a) and up to 8 weeks b)

CONCLUSION

The results obtained within this study contribute to the establishment of some peculiarities of thermal behavior and the shape-memory effect of the archwires. We have demonstrated that after a prolonged period of time in the patient's month, the archwires have no significant changes in the proportion of elements in the tested wires: Ni – 54.36 +/– 0.8 wt% and Ti – 45.64 +/– 0.8 wt%. The DSC analyses made in the temperature range from –50°C to +50°C and back to –50°C, indicate that Ms temperature for as-received sterilized and used archwires is below –30°C. The results will be useful for clinicians to make a choice for using the proper archwire during treatment.

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ОХАРАКТЕРИЗИРАНЕ НА СТРУКТУРАТА И МОРФОЛОГИЯТА НА ТОПЛОАКТИВИРАЩИ НИКЕЛ-ТИТАНОВИ ОРТОДОНТСКИ ДЪГИ

И. Илиевска[1*], В. Петров[2], Л. Андреева[2], Д. Ковачева[3], А. Залески[4], М. Дрозд[4], Е. Буковска[4], В. Микли[5], А. К. Стоянова-Иванова[1]

[1] *Институт по физика на твърдото тяло „Акад. Георги Наджаков“, Българска Академия на Науките*

[2] *Факултет по дентална медицина, Медицински Университет – София, бул. „Св. Георги Софийски“ 1*

[3] *Институт по обща и неорганична химия, Българска Академия на Науките*

[4] *Институт по ниски температури и структурни изследвания, Полска Академия на Науките*

[5] *Център за изследване на материали към Талински Технологичен Университет – Талин, Естония*

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(Резюме)

Топлоактивиращите никел-титанови (Ni-Ti) ортодонстки дъги са широко използвани в първия етап на ортодонтското лечение. Направени са от сплави които проявяват свойството памет на формата, което се свързва с мартензитна трансформация, проявяваща се при промяна на температурата или механично въздействие (стрес). Целта на това изследване е да се охарактеризира структурата, химичния състав и температури на фазовите преходи на топлоактивиращи никел-титанови ортодонтски дъги при редовната употреба.

За тази цел, три вида топлоактивиращи никел-титанови (Ni-Ti) ортодонстки дъги с размери 0.016“ x 0.022“ (0.406 x 0.558 mm) бяха изследвани: неизползвани (фабрични), неизползвани автоклавирани и използвани по време на лечение, произведени от фирмата 3M Unitek, Монровия, Калифорния, САЩ. Анализите са проведени със следните методи: рентгеноструктурен анализ (XRD), сканираща електронна микроскопия (SEM), рентгенов микроанализ (EDX) и диференциална сканираща калориметрия (DSC).

Рентгеноструктурният анализ направен при стайната температура показва типични пикове за Ni-Ti сплав с аустенитна тип структура. Фазовите преходи са изучавани с метода на диференциална сканираща калориметрия при температура от –50°C до +50°C. Показвано е че при Ni-Ti топлоактивиращи дъги освен аустенит към мартензит преход, има наличие и на междинна R фаза. При процеса нагряване (–50°C до +50°C) тремична фазова транформация се наблюдава при ~12°C. Не са регистрирани допълнителни ендотермични/екзотермични ефекти. При процеса охлаждане, DSC резултатите показват термични фазови преходи при около 10°C се наблюдава формиране на R-фаза, докато при около –40°C, Ni-Ti структура се трансформира до мартензит.

Резултатите получени от енергийно-дисперсионния анализ показват че няма значителни промени на химичния състав на повърхността на изследваните дъги. Сканиращата електронна микроскопия показва промени в морфологията на дъгите след клинично им използване.

Резултатите получени в хода на изследването допринасят за установяване на някои особености в термичното поведение и ефекта на запаметяване на формата на изследваните дъги.