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DEPOSITION OF CHITOSAN LAYERS ON NiTi SHAPE MEMORY ALLOY

OSADZANIE WARSTW CHITOZANU NA POWIERZCHNI STOPU NiTi WYKAZUJĄCEGO PAMIĘĆ KSZTAŁTU

The NiTi shape memory alloys have been known from their application in medicine for implants as well as parts of medical devices. However, nickel belongs to the family of elements, which are toxic. Apart from the fact that nickel ions are bonded with titanium into intermetallic phase, their presence may cause allergy. In order to protect human body against release of nickel ions a surface of NiTi alloy can be modified with use of titanium nitrides, oxides or diamond-like layers. On the one hand the layers can play protective role but on the other hand they may influence shape memory behavior. Too stiff or too brittle layer can lead to limiting or completely blocking of the shape recovery. It was the reason to find more elastic covers for NiTi surface protection. This feature is characteristic for polymers, especially, biocompatible ones, which originate in nature. In the reported paper, the chitosan was applied as a deposited layer on surface of the NiTi shape memory alloy. Due to the fact that nature of shape memory effect is sensitive to thermo and/or mechanical treatments, the chitosan layer was deposited with use of electrophoresis carried out at room temperature. Various deposition parameters were checked and optimized. In result of that thin chitosan layer (0.45μm) was received on the NiTi alloy surface. The obtained layers were characterized by means of chemical and phase composition, as well as surface quality. It was found that smooth, elastic surface without cracks and/or inclusions can be produced applying 10V and relatively short deposition time – 30 seconds.

Keywords: surface modification, chitosan, NiTi, shape memory

Stopy NiTi wykazujące pamięć kształtu znane są ze swych zastosowań w medycynie na implanty oraz części urządzeń medycznych. Jednakże, nikiel należy do rodziny pierwiastków o toksycznym działaniu. Oprócz faktu, że jony niklu są związane z tytanem w fazę międzymetaliczną, ich obecność może powodować alergię. W celu ochrony organizmu przed uwalnianymi jonami niklu powierzchnia stopu NiTi może być modyfikowana z wykorzystaniem azotków tytanu, tlenków lub warstw diamentopodobnych. Z jednej strony warstwy mogą odgrywać rolę ochronną, ale z drugiej strony mogą wpłynąć na zachowanie pamięci kształtu. Zbyt sztywna lub zbyt krucha warstwa może prowadzić do ograniczenia lub całkowitego zablokowania odzysku kształtu. Był to powód, aby znaleźć bardziej elastyczne pokrycia zabezpieczające powierzchnię NiTi. Ta cecha jest charakterystyczna dla polimerów, zwłaszcza biokompatybilnych polimerów pochodzenia naturalnego. W omawianym artykule zastosowano chitozan jako osadzaną warstwę na powierzchni stopu NiTi, wykazującego pamięć kształtu. Ze względu na fakt, że natura efektu pamięci kształtu jest wrażliwa termicznie oraz na obróbkę mechaniczną, warstwa chitozanu została osadzona z wykorzystaniem elektroforezy przeprowadzonej w temperaturze pokojowej. Sprawdzano i optymalizowano różne parametry osadzania. W rezultacie otrzymano cienką warstwę chitozanu (0.45μm) na powierzchni stopu NiTi. Uzyskane warstwy scharakteryzowano pod względem składu chemicznego i fazowego jak również jakości powierzchni. Stwierdzono, że gładka, elastyczna powierzchnia, bez pęknięć i/lub wtrąceń może być uzyskana stosując napięcie 10V i stosunkowo krótki czas osadzania – 30 sekund.

1. Introduction

Due to unique properties, NiTi shape memory alloy belongs to the qualitatively new group of biomaterials frequently used in medicine [1]. They can be applied for production of medical devices or its part such as: stents, staples, orthodontic wire, orthopedic implants, guide wires, jaw implants, surgical instruments, etc. [2]. Apart from good biocompatibility and corrosion resistance of NiTi alloys in body fluids, there are still controversies of using them for long-term implants. These concerns relate to the presence of nickel, which consti-

tutes about 50% of the chemical composition. However, the nickel in these alloys is present in a bounded form. Nickel in free form is known from its toxicity and carcinogenicity. Its can cause allergies in susceptible individuals [3]. One way of protect against migration to the surface of nickel ions and their penetration into the human body is a surface modification of NiTi alloys. Numerous literature data report method and technique for human body protection against migration of nickel ions from implants [4-6]. In the case of NiTi alloys, the surface modification can be done by application of protective layers or coatings maid from biocompatible materials, while

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maintaining the properties of the shape memory effect. The most commonly used materials are titanium nitrides, titanium oxides, diamond-like layers, apatite or biopolymer coating [4-11]. The layers lead to improvement of biocompatibility, corrosion resistance and reduce adhesion of bacteria as well as biofilm formation. However, most of techniques used in the deposition of layers require an increase of processing temperature above one of parent phase decomposition to equilibrium phases. Thus the shape memory effect can be spoiled [4]. Apart from the material used, important role plays thickness of deposited layer. Too stiff and/or too brittle layer can lead to limiting or completely blocking of the shape recovery. In order to overcome all these inconveniences there is still looking for new non-conventional coating techniques NiTi alloys. One of them may be electrophoretic deposition. The deposition may be done at temperature, that does not exceed 100-200°C [12]. In comparison to other techniques it is an universal method, easily adapted for specific applications. In the biomedical engineering is also used for the preparation of SiO_2 or hydroxyapatite layers [12].

Another important aspect applying of the biopolymer coating on the surface of NiTi alloys is the ability to deliver the drug accelerating adoption of the implant in the human body. In this case, layers can be made from biodegradable polymer. Polylactide and chitosan belong to this group. Chitosan is a derivative of chitin. Due to its non-toxicity and biodegradability, it becomes widely used in medicine, veterinary medicine, cosmetics or the wider biotechnology [13].

In reported paper, the chitosan was applied for layer deposited on surface the NiTi shape memory alloy. Chitosan was deposited on NiTi alloy applied electrophoresis. Obtained coatings were characterized by means of chemical and phase composition and surface quality. Also assesses their impact on the martensitic transformation was considered.

2. Materials and experimental procedures

The substrate used for the electrophoretic deposition of the chitosan layers was the NiTi shape memory alloy with nominal chemical composition: 49.4at.% Ti and 50.6at.% Ni. The NiTi alloy was prepared in rectangular samples with dimensions of 15 mm×10 mm×1 mm. Initially, the samples were mechanically polished with SiC papers down to 2000 grit. Next, diamond suspensions, up to 1 μm, were used. The final treatment, to achieve a mirror-like surface, was done using 0.1 μm colloidal silica suspension. Then, all samples were ultrasonically cleaned for 20 min using acetone and next immersed in the HCl solution (v/v 1:1) for depassivation of the substrate.

A commercial medium molecular weight chitosan powder (MW = 80kDa) with the degree of deacetylation of 75-85%, and the acetic acid were purchased from Sigma-Aldrich. The process of deacetylation of chitin was extracted from red crabs. The chitosan layers were deposited on the NiTi substrate by cataphoresis from 1% (v/v) aqueous acetic acid solution in which 1g/dm^3 of chitosan powder had been dissolved at room temperature. Nanopure water (Milli-Q, 18.2 MΩ cm^2) was used for the preparation of the solution. Before electrophoretic deposition, the electrolyte was stirred magnetically for 24h

to achieve a clear solution. The layers were obtained electrophoretically using a MAG-5N galvanizing aggregate at a voltage of E = 4 and 10V at different time of deposition ranging from 30 to 600s. The electrochemical cell included the NiTi plate, which was the cathode placed parallel to the Pt foil, and which served as a counter electrode. The distance between the cathode and anode was 15 mm. After electrophoretic deposition, the chitosan/NiTi layers were rinsed with Milli-Q water, dried for 48h and weighed.

Observations of the surface of chitosan layers were performed using JEOL JSM-6480 scanning electron microscope (SEM) equipped with Energy Dispersive Spectrometer (EDS). Phase analysis was done on the base of X-ray diffraction patterns (XRD) measured with use of diffractometer X'PertPro. Measurements were done using monochromatized Cu Kα radiation at room temperature. The X-ray grazing incidence diffraction (GIXD) technique was used for studies of the thin films. The X-ray diffraction patterns were measured at incidence angles (α) of 0.2, 0.3, 0.5 or 1.0°. Initial state of NiTi alloy as well as chitosan was characterized basing on X-ray diffraction pattern measured in classical Bragg Brentano geometry.

The influence of the electrophoretic deposition of the surface layers on the course of the martensitic transformation was determined from thermograms obtained during the heating and cooling (calorimeter DSC 1 Mettler Toledo). Samples were tested in the temperature ranged from -100°C to +100°C at a heating/cooling rate of 10°C/min.

3. Results and discussion

3.1. Materials before deposition

NiTi alloy was quenched from 800°C to ice-water. In this state, the characteristic temperature – A_f was below 0°C (Fig. 1). Thus, at room temperature, alloy possesses structure of the parent phase (B2) (Fig. 2).
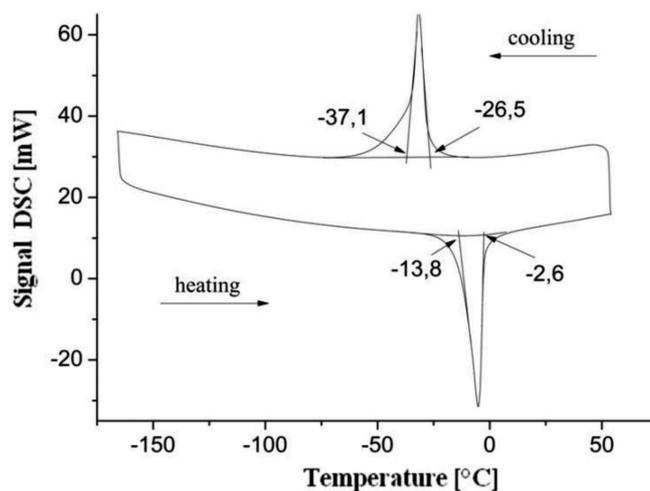

Fig. 1. DSC cooling/heating curves measured for NiTi alloy after quenching from 800°C

Thermal behavior of chitosan was studied over temperature range from -100°C up to 200°C (Fig. 3). The heating curve shows only one broaden thermal peak with its mini-

mum at 92°C. The transformation starts at 34°C and ends at 137°C. This effect may be related to the loss of water during the preparation of chitosan.
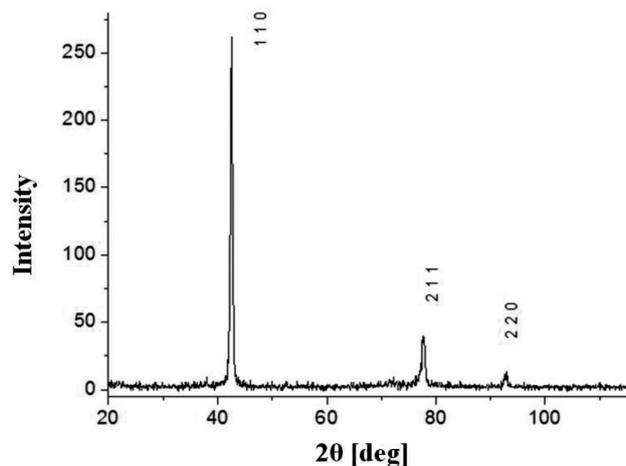

Fig. 2. X-ray diffraction pattern of the NiTi alloy before electrophoretic deposition
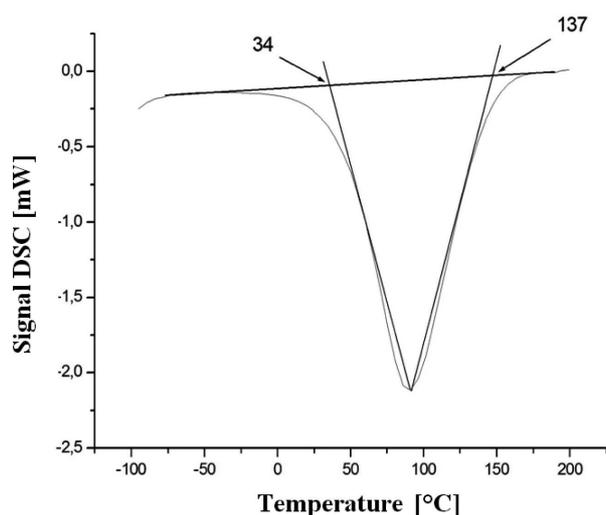

Fig. 3. DSC heating curve measured for chitosan before its electrophoretic deposition
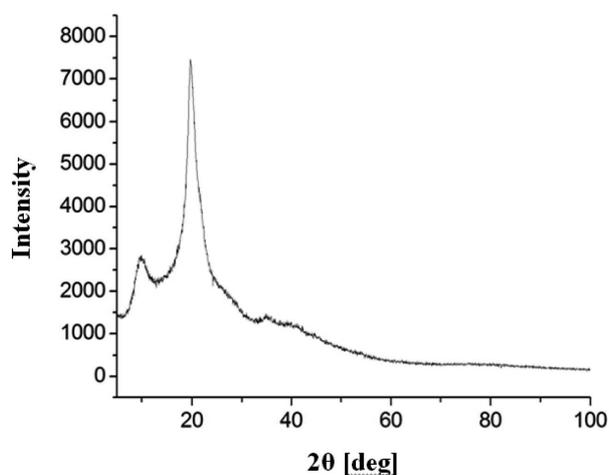

Fig. 4. Diffraction pattern of the chitosan before electrophoretic deposition

X-ray diffraction pattern measured for powdered chitosan is shown in Figure 4. Half-widths of the diffraction lines take value of about 2.3 degrees 2θ. Due to the crystallographic system (orthorhombic) and a relatively high value of the unit cell parameters a_0 = 11.87 [Å], b_0 = 14.72 [Å], c_0 = 10.42 [Å] the strongest diffraction lines lie in a short distances. It creates an impression that chitosan powder is amorphous.

3.2. NiTi alloy after chitosan deposition

The analysis of the phase composition of the chitosan layers was carried out using the Grazing Incidence X-ray Diffraction (GIXD) technique. In general, the diffraction patterns obtained for all samples revealed the presence of diffraction lines, which belong to chitosan or to the B2 parent phase (Fig. 5). However, intensities of measured diffraction lines differs from that observed for these materials before deposition. The first of all, for the B2 phase only the strongest line 011 can be observed. Its position still remains the same value. Also, in comparison to the intensities of chitosan's line, decrease of α angle caused decrease of the intensity of the B2 phase diffraction lines. It can be evidence that amount of the B2 phase decreases in the penetration area of the X-ray beam. Moreover, character of the diffraction lines of chitosan has changed. Diffraction patterns showed presence only two lines, which belong to chitosan. However, their half-width exceeded 10° of 2θ. These lines also differ in the intensity in relation to the diffraction pattern measured for a chitosan before its deposition (Fig. 4). After chitosan deposition, the first line possessed higher intensity in comparison to the second one. Additionally, both chitosan's lines increased their half-width. This character of diffraction pattern indicates that deposited chitosan is completely amorphous. Similar behavior showed diffraction patterns measured for all samples with deposited chitosan's layer.

Figures 6, 7 and 8 show SEM images of the surface of the films prepared under various conditions of voltage and deposition time. Low value of voltage (4V) and deposition time 600s caused formation of the uniform, amorphous layer of chitosan (Fig. 6). On the surface of layer are visible traces of hydrogen bubbles formed during electrophoretic deposition process.
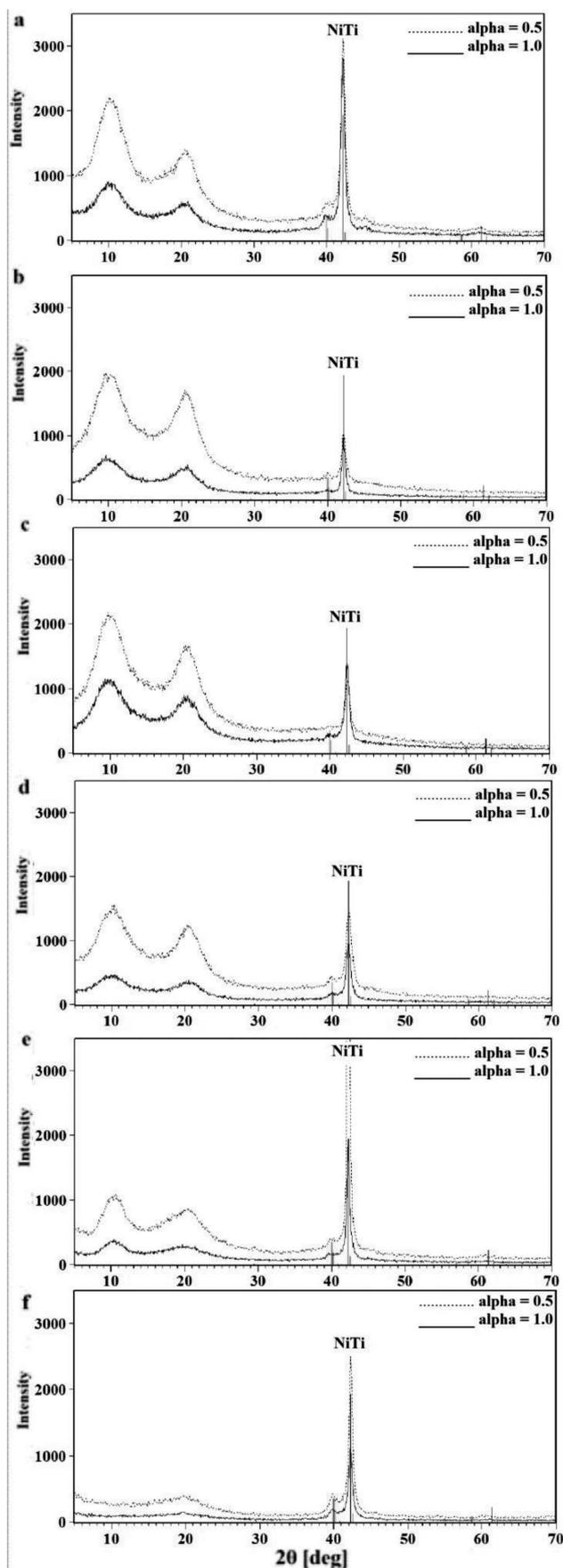
Fig. 5. Set of diffraction patterns measured using a Bragg-Brenttano geometry and GIXD technique for samples: (a) 4V/600s, (b) 10V/600s, (c) 10V/300s, (d) 10V/120s, (e) 10V/60s, (f) 10V/30s
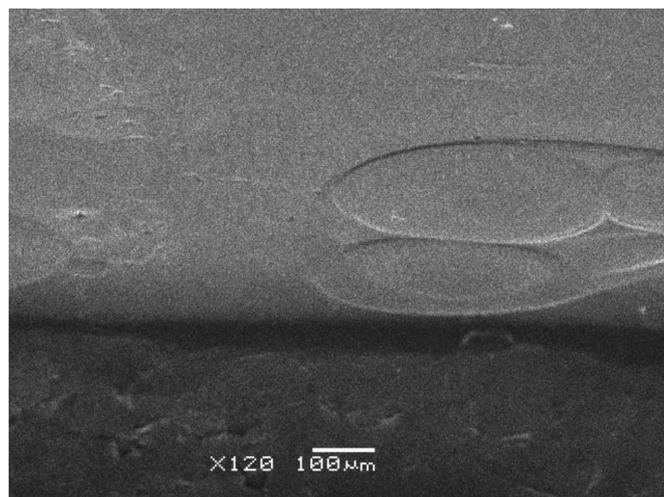

Fig. 6. SEM image of chitosan layer prepared at 4V for 600 s

The increase of the deposition voltage up to 10V leaded to the increase in intensity of the electrophoretic deposition process. The result is the increase in the amount of hydrogen bubbles emitted during electrophoresis. This caused a significant discontinuity of the formed chitosan layer (Fig. 7).

The best quality of the chitosan layer in terms of its uniformity and continuity was obtained by reducing the deposition time to 30 seconds while maintaining the voltage at 10V. Surface of the chitosan layer was distinguished itself of uniformity and there was found no presence of residues of the secreted hydrogen. Both the central area and the sides of the sample were evenly coated with chitosan (Fig. 8).

Influence of the deposition parameters on the chitosan layers quality was determined by measuring the roughness and thickness. Measurements were performed for samples with the chitosan layer deposited with a voltage of 10V of different deposition time.
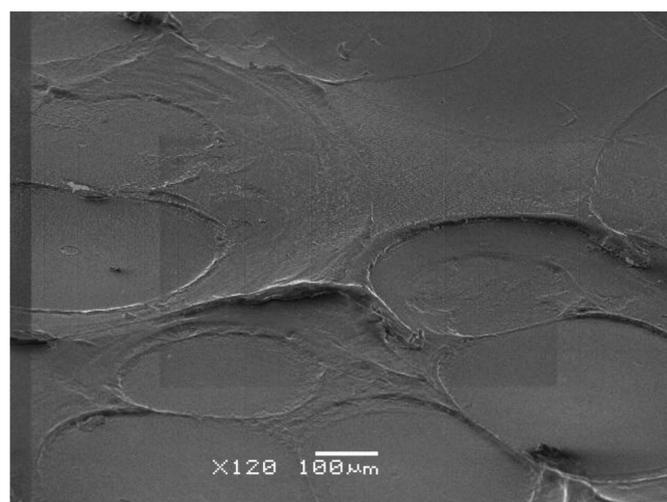

Fig. 7. SEM image of chitosan layer prepared at 10V for 600s

The surface roughness was evaluated based on the analysis of the surface profiles measured over a length of about 7.5 mm, in the different locations of the samples. Figure 9 illustrates an exemplary profiles measured on surface of the chitosan layers deposited for 30 and 600sec.
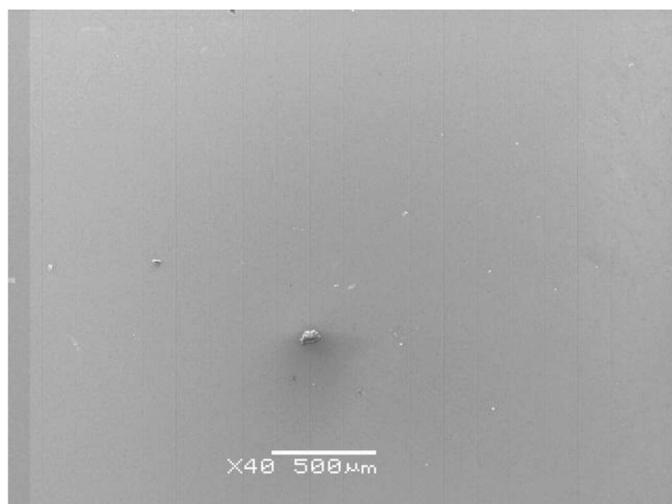
Fig. 8. SEM image of chitosan layer prepared at 10V for 30s

Measurements of profiles allowed to determine the arithmetic average of the absolute value, R_a and average distance between the highest peaks, R_z (Tab. 1). The values of R_a and R_z very well correlate with the results of the microscopic observations. Decreasing of the amount of surface irregularities resulting from the release of hydrogen evolution during the electrophoretic deposition process reduces the surface roughness. The measured profile for the chitosan layer deposited for 600s showed the significant deviation from the assumed average level (Fig. 9a). At these points height of the inequality reaches values up to 55 μm. They come from bubbles of evoluted hydrogen. As a result, for the chitosan layer of short deposition time 30s value of R_a is less than 0.1 μm and height of the inequality 0.3 μm (Fig. 9b). Reducing of the deposition time has led to a reduction of the chitosan layer roughness.
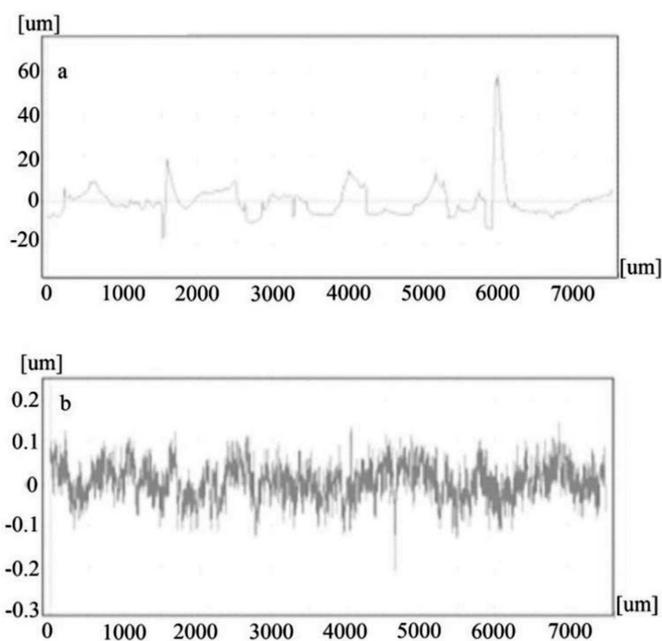

Fig. 9. Examples of measured profiles for chitosan layers depositeds in time: (a) 600 s and (b) 30 s

From the measurements of GIXD method, in which the diffraction pattern depend on the penetration depth of X-rays resulted of relationship between the parameters of deposition the chitosan layer and its thickness. The thickness measurements were carried out using the profilometer by measuring the difference between the surface of the chitosan layer and the surface of the NiTi substrate. The measurement was performed at 10 different sites along the shorter side of the plate. The results are presented as average values in Table 1 and Figure 10. The thickness of the chitosan layer increases with increasing deposition time from about 0.5μm to 12μm. Standard deviation value is also important, which for longer times takes a value to 20%. This fact further confirms the growth of the surface of the chitosan layer roughness as the lengthening the deposition time.

TABLE 1

Characteristics of roughness and thickness of the deposited chitosan layer on the surface of NiTi alloy

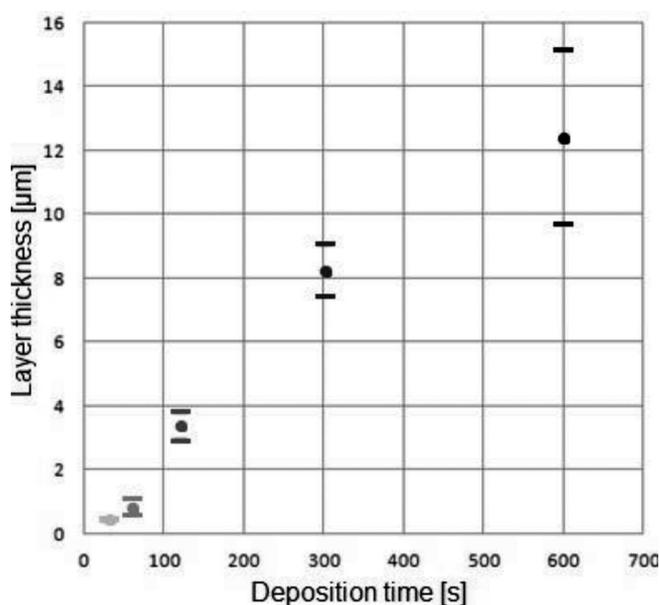| Voltage [V]	Deposition time [s]	R_a [μm]	R_z [μm]	Average thickness [μm]	Standard deviation [μm]
10	600	5.1	32.1	12.41	2.72
10	300	2.5	24.7	8.28	0.82
10	120	0.9	3.8	3.41	0.44
10	60	0.4	0.4	0.86	0.26
10	30	0.04	0.3	0.45	0.04

Fig. 10. Dependence of chitosan layer thickness on the substrate NiTi from deposition time

Influence of the electrophoretic deposition on the course of the martensitic transformation was studied with use of DSC. Example of DSC cooling/heating curves measured for deposited sample at 4V/600s and 10V/600s are shown in Figure 11. All measured DSC thermograms revealed presence of the one-step reversible martensitic transformation. From obtained curves the characteristic transformation temperatures were determined (Table 2). The values of characteristic temperatures, for samples after chitozan deposition, were similar. However, in comparison to those determined for the NiTi alloy

before electrophoretic deposition of chitosan layer characteristic temperatures of the forward transformation were shift of about 9 degrees in region of lower temperature. Temperatures of the reverse martensitic were comparable to ones measured for as-cast sample. In general, electrophoretic deposition cause a slight lowering of the characteristic temperatures of the martensitic transformation. It can be considered as an advantage. The gap between human body temperature and characteristic for martensitic transformation can be a measure of the security. Increase of the gap causes increase standards of safety when NiTi with chitosan have been applied as material for implants.
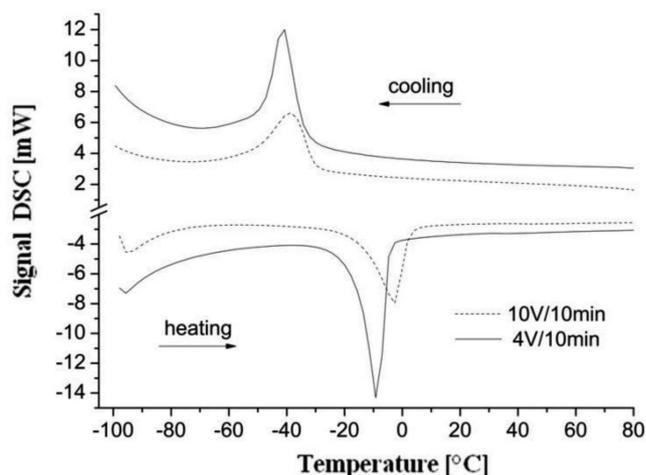

Fig. 11. Thermograms of the samples with chitosan layer deposited in time 600s at voltage 4V (a) and 10V(b)

TABLE 2

Characteristic temperatures for the samples NiTi before and after electrophoretic deposition of chitosan layers

Sample	M_s	M_f	A_s	A_f
NiTi	-26.5°C	-37.1°C	-13.6°C	-2.6°C
NiTi + layer E=4V, t=600s	-33.77°C	-48.54°C	-15.84°C	-5.13°C
NiTi + layer E=10V, t=600s	-30.3°C	-53.1°C	-15.0°C	+1.7°C

4. Conclusion

Electrophoretic deposition of protective chitosan layers appears to be useful method of coating the surface of NiTi alloy. This method is simply and does not require sophisticated equipment. By properly adjusting the voltage and deposition time, it is possible to control the thickness and uniformity of the formed layers.

The use of a relatively low voltage and long deposition time, allow obtaining a homogeneous chitosan layer of a very similar thickness on the whole surface. Increase in the voltage up to 10V with a longer deposition time leads to intensification of the process of electrophoresis. This causes an increase in the amount of evoluted hydrogen. This effect is not indifferent for the forming of the chitosan layer. It blocks the flow of chitosan particles to the surface of the samples, which strongly affects on the topography of the chitosan surface - the layer becomes rough, and even cracking and peeling of fragments of the chitosan from the substrate occur.

The use of shortened deposition time but at a higher voltage, leads to uniformity of surface topography and reduce the roughness of the chitosan layer. Also, the impact of hydrogen evolution on the deposited layer is lower and therefore effects of this interaction are smaller. Application of the chitosan coating with shortened deposition time to 30 seconds has enabled to obtain a uniform layer having a smooth and uniform surface with low roughness.

Results of the DSC showed that the deposited layer and the electrophoretic deposition conditions that have been used, they do not influence on the course of martensitic transformation of NiTi alloy. Also, they will have not negative effect on the shape memory effect.

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