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Study on bioactivity of NiTinol after surface treatment

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ABSTRACT

Purpose: The aim of the work was to assess bioactive properties and corrosion resistance of nickel titanium alloy after alkali treatment and spark oxidation in Hank's Balance Salt Solution.

Design/methodology/approach: Surfaces of samples were prepared by chemical treatment in NaOH followed by heat treatment, and spark oxidation. Corrosion resistance was investigated using potentiodynamic method. Chemical composition of the samples surface was measured using SEM EDX. Surface roughness and topography was analyzed using AFM. Bioactive properties were analyses on the basis of the chemical composition of the samples immersed in HBSS for 14 days.

Findings: The chemical composition analysis of the samples showed that alkali treatment increased significantly nickel content in top layer and also increase in roughness was observed. Spark oxidation results also in roughness increase. Corrosion test showed insignificant increase of the corrosion resistance after oxidation while alkali treatment caused drop of the resistance. Bioactivity study revealed that both applied treatments did not improve bioactive properties of the NiTinol when compared with simply ground samples.

Research limitations/implications: Two types of the treatment applied for nickel titanium and intended to improve bioactive properties were investigated. There was no improvement in bioactivity observed after surface treatment. However, alternation in chemical composition, corrosion resistance, and topography were observed. Further analysis of biocompatibility and mechanical properties are required.

Practical implications: Both chemical and electrochemical treatment, as presented in the paper, gave promising results in terms of wetting ability, topography and apatite film formation, however further study are required to confirm suitability of the treatments for medical applications.

Originality/value: The obtained results revealed unsuitability of the alkali treatment intended to improve bioactivity of the Nitinol. Nevertheless, obtained results for spark oxidised samples were found promising in terms of the chemistry and topography and further biological studies are planned.

Keywords: Nickel titanium; Spark oxidation; Bioactivity; AFM; XPS; Corrosion resistance

MATERIALS

1. Introduction

Nickel titanium alloy has been attaching a lot of attention due to its mechanical properties; superelasticity or shape memory effects. This type of the shape memory alloys are currently used in cardiovascular, urological, tracheal and dental applications due to their unique mechanical properties. These mechanical properties are driving research into orthopaedic applications. Today only a few cases have been reported where Ni-Ti alloy was used in orthopaedics.

However, despite of favourable mechanical properties very high nickel content causes concern. Use of nickel-titanium alloy entails risk of nickel release. Nickel is essential element in human body, however when the threshold for daily digestion 200-300μg [1] is exceeded it causes sever immunological problems. In addition corrosion (pitting, crevice), wear of the devices could increase nickel, titanium concentration and cause appearance of metal debris in surrounding tissues causing abnormal tissue reactions. For these reasons there are a lot of studies and attempts, in one hand to improve tribological and corrosion properties [2-6], and in the other hand to improve biocompatibility of the material [7-11]. Nevertheless, some of the coatings such as Diamond Like Coating (DLC), that has a very positive effect on nickel release, wear properties, and low implant reactivity in the body [5], could cause severe corrosion problems when this coating is impaired. As is well known, from an electrochemical point of view, a combination of two materials with a completely different electrochemical potential will give rise to very fast corrosion of the material [12,13].

In order to improve the osteological response to the implants it is desirable to enhance the bioactivity of the alloy surface. Positive results for Ni-Ti bioactivation were achieved by thermal treatment [15], passivation in nitric acid [16] and combined H_2O_2 and NaOH treatment [17]. However, the rate of nickel release from such treatments can be increased undesirably [18]. The primary aim of this study was to compare different surface treatments used in the bioactivation of pure titanium surfaces – thermal, alkali treatment and spark oxidation and assess their suitability as treatments for Ni-Ti alloys by examining the surface properties.

2. Materials and methods

In the study nickel titanium alloy was used in the superelastic form. Flat samples were ground on SiC paper to 4000 grit and cleaned, soaked in HNO_3 for 10 min and cleaned again. Then samples were prepared in the following ways:

- alkali treated – 10M NaOH (24h, 80°C) then heat treatment in 600°C in air,
- oxidised using plasma electrolysis method in H_2SO_4, H_3PO_4, 250mA, 1 min [19].

As a reference samples, ground NiTi was used. The topography of the samples surfaces was examined using atomic force microscopy (AFM) (PSIA XE-100) in non-contact mode. SEM EDX (Stereoscan 90B Scanning electron microscope Cambridge instruments Ltd., UK) was used to examine chemical composition of the sample surfaces. To assess wettability of the surfaces the Contact Angle (CA) (KSV Cam200) measurements were carried out using ultrapure water. To assess ability for calcium and phosphorous precipitation on the surface sample were immersed in HBSS for 14 days.

The pitting corrosion resistance was analysed on the basis of recorded anodic polarization curves. The VoltaLab® (PGP 201 system by Radiometer) for electrochemical tests was utilized. As the reference electrode saturated calomel electrode (SCE) was used, the auxiliary electrode was platinum electrode. The recording of anodic polarization curves was carried out from potential value $E = E_{corr} - 100$ mV with polarization in direction of positive values and with the potential changes rate equal to 1mV/s. When the current density has achieved the value of $1mA/cm^2$ the direction of polarization was changed and the returned curve has recorded. On the basis of the obtained curves the breakdown potentials E_b, polarization resistance R_p, corrosion current density i_{corr} and corrosion rate have been determined.

The investigations was carried out for the samples in HBSS at 37±1°C and pH = 7.2.

3. Results

The AFM study showed that both alkali treatment and spark oxidation altered topography of the surface – Fig. 1.

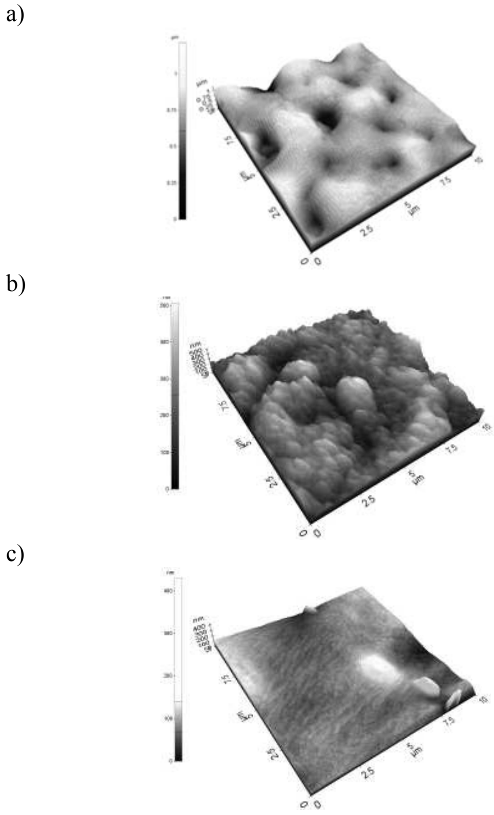

Fig. 1. AFM images of the (a) spark oxidised and (b) alkali treated, (c) ground NiTi

The spark oxidized samples had rough layer exhibiting a pitted structure – Fig.1a. Alkali treatment caused also roughness increase (assessed on the basis of the peaks height) - Fig. 1b. Ground surface were smooth – Fig. 1c

The SEM EDX results are compiled in table 1. The study revealed significant differences in the chemical composition of both treated samples. Moreover, the alkali treatment resulted in a very low contact angle. The contact angle values were significantly lower for both treated samples when compared with ground samples, and were respectively 14 and 12° for alkali treated and spark oxidised.

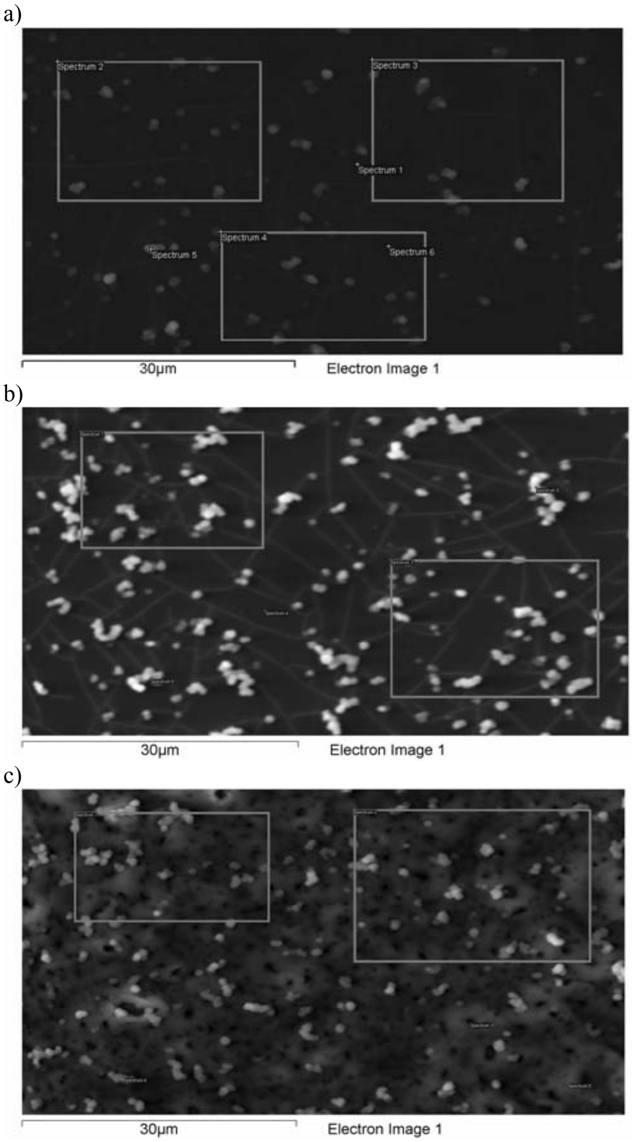

Fig. 2. SEM images of: a) ground, b) alkali treated and b) spark oxidised nickel-titanium after 14 day immering in HBSS

After 14 days of immersing in HBSS increase of calcium and phosphorous on the surfaces was observed for all the samples. The ratio Ca/P for ground samples was around 0.85. For alkali treated samples Ca/P ratio was greater – 0.95, while for spark oxidised was significantly lower – 0.29 (Table 1). This could be the reason of high initial phosphorus content in the layer (12%) which counted to the total amount of detected element Is spite of the relatively quick increase of Ca content on all the tested samples the ratio was far from expected HAP ratio 1.67. The growth of the apatite film on the surface was similar to observed in the previous study for bioactive Ti [21].

Table 1.
Results of chemical composition of nickel titanium, as obtained from SEM EDX, before and after immersing the samples in HBSS for 14 days

	Ca, %	Ca/P	Ni/Ti	CA,°
NT	n/a	n/a	1.02	32.71 ±0.44
NT14days	3.2 ±0.89	0.85 ±0.07	0.99 ±0.09	n/a
BNT	n/a	n/a	0.51 ±0.11	14.52 ±3.09
BNT 14days	3.27 ±0.89	0.97 ±0.09	0.34 ±0.03	n/a
SP	n/a	n/a	0.47 ±0.02	12.25 ±6.20
SP 14 days	3.62 ±0.65	0.29 ±0.02	0.41 ±0.06	n/a

Results of electrochemical tests have revealed the influence of surface preparation of the Ni-Ti alloy on the corrosion resistance – Table 2.

Table 2.
Results of pitting corrosion resistance

Sample	$E_{corr.}$, mV	E_{tr}, mV	$i_{corr.}$, nA/cm^2	R_p, kΩcm^2	Corr., µm/year
1 (SP)	-80	+1422	40.24	646	0.46
2 (NT)	-290	+1362	59.22	439	0.68
3 (BNT)	-236	+1121	62.20	418	0.71

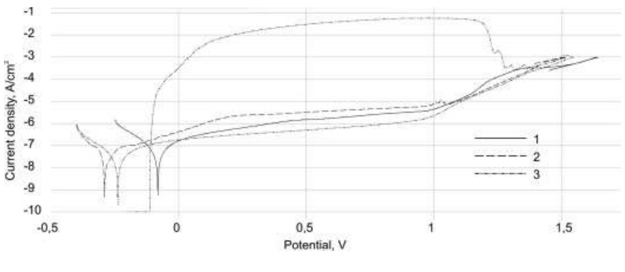

Fig. 3. Anodic polarization curves recorded for ground, alkali treated, and spark oxidised samples

For spark oxidised (SP) samples, the corrosion potential was in the range E_{corr} = -83 – -77 mV – Table 2. Polarization of samples caused the increase of anodic current for potentials in the range E_{tr} = +1410 – +1434 mV – Fig. 2. Polarization resistance of the samples was equal to R_p = 646 kΩcm^2. The tests have revealed that for the ground samples (NT) the corrosion potential was in the range E_{corr} = -300 – -280 mV and the average value of the polarization resistance was R_p = 439 kΩcm^2 – Table 2. The recorded curves of the anodic polarization were characterized by the further increase of the anodic current density in the passive range – Fig. 3. Polarization of the samples in direction of positive values of the potential caused the increase of the current density for potentials in the range E_{tr} = +1350 – +1374 mV. The lowest values of transpassivation potential, current density anodic and polarization resistance were observed for the alkali treated (BNT) samples - Table 2. Anodic polarization curves recorded for the sample were characterized by hysteresis loop in the passive range that indicates lack of pitting corrosion resistance - Fig. 3.

4. Conclusions

Large differences in topography, chemistry and wettability of modified Ni-Ti surfaces were observed. Bioactivity study showed gradual increase of the film along study for all the samples. However, differences in Ca/P ratio for different surface preparation were observed. The rate of the film growth and Ca/P ratio was the most favorable for ground NiTi and alkali treated, which was comparable for bioactive Ti [14]. Corrosion resistance of metallic biomaterials is one of the basic criteria determining their usefulness. Problems of corrosion resistance of NiTi alloy in simulated body fluids are not well recognized. The analysis of the pitting corrosion results shows the favorable influence of the suggested surface treatment (SP). On the basis of the research it can be stated that corrosion behavior of implants should be considered with respect to the appropriate environment of body fluids. In order to fully characterize the corrosion resistance of the analyzed alloy in simulated body fluids, stress and fatigue corrosion test should be carried out.

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