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Highly improved Nitinol biomaterial devices by magnetoelectropolishing (MEP)

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ABSTRACT

In recent years, the use of Nitinol as a metallic biomaterial being compound of nickel and titanium, has been steadily growing, particularly in medical and dental devices markets. However, further application of Nitinol has been slowed down due to leaching nickel and unavoidable inclusions appearing on the surface during manufacture of this intermetallic compound. Electropolishing of Nitinol biomaterial samples as-received (AR) was carried out under different conditions: (a) on the *plateau* level (EP), (b) above the *plateau* (EP+), and (c) in the magnetic field (MEP). This work is to present magnetoelectropolishing (MEP) as an electrochemical processing method able to significantly improve the Nitinol biomaterial properties. Following our previous SEM/EDS studies, and corrosion resistance improvement of Nitinol, in this work XPS and XRD study methods were used. First of all, as indicated by XPS study results concerning biocompatibility, it was proved that MEP leaves Nitinol surface enriched in oxygen and with nickel reduced to zero. Thus the titanium oxides, generally TiO_2, are formed on Nitinol surface. It appears that by introducing a magnetic field into the electrolysis system, another effect relying on a considerable increase of Nitinol mechanical properties is obtained. The experiments carried out on surgical needles show an unusual multiple growth in resistance to bending until fracture. Further increase in fatigue resistance is usually limited by different size of

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inclusions which happen to appear on the Nitinol part surface. Moreover, in this work also a simple method is proposed to reject the Nitinol parts, with the inclusions detected on the biomaterial surface, before their application.

***Keywords*:** Nitinol biomaterial, Fatigue resistance, XPS, Surface roughness, Biocompatibility, magnetoelectropolishing

1. INTRODUCTION

Nitinol as a shape memory alloy is remarkable material opened upon a wide range of uses. In fact, Nitinol is an intermetallic compound formed of nickel and titanium. Some of its major applications are in medicine to produce medical implants, tools and devices. The very good ductility and malleability allow the material to be produced in many forms such as: wires, tubes, sheets, needles, rods or bars. Excellent ductility allows Nitinol to be drawn as wires and tubes with such small outer and inside diameters that they can be used in production of microscopic vascular devices utilized in treating vasculature of brain. Nitinol's unique properties allow for minimally invasive surgical operations using stents and medical implants in view of improving quality of life for patients [1-3].

Presently used melting methods, sort of raw materials and manufacture techniques do not allow for obtaining flawless Nitinol material [4]. In fact its manufacture results in unavoidable cross-sectional impurities, leading to the formation of non-metallic inclusions on the surface; moreover, they are critical to control. The elements, such as oxygen, nitrogen and carbon, present in the melt form titanium oxides, nitrides, and carbides, respectively. One of the inclusions, TiC tends to be small, uniform, and evenly distributed, whereas $Ti_4Ni_2O_x$ intermetallic oxides are blocky and unevenly distributed [4, 5]. They are hard inclusions acting as discontinuities in the matrices so this is why Nitinol is under investigation and the subject of continuous studies [3-8]. Unfortunately these flaws affect the fatigue strength leading to device failure.

Corrosion resistance and inertness of Nitinol in a variety of environments, as well as its shape memory effect, bring about the use of this intermetallic compound of nickel and titanium. Utilization of this biomaterial has been constantly growing, particularly in medical and dental devices markets (e.g. endodontic files, reamers, etc.). However, broader and further application of Nitinol as biomaterial has been slowed down by two factors:

- a very high nickel content (over 50%)
- the role of inclusions, which presently are unavoidable in this intermetallic compound [3-11].

Biomaterial surface alteration, which must include the influence of sterilization on the biomaterial, is the very important way to tailor post implantation interaction between biomaterials and biomolecules adsorption and further cellular processes [12-15].

The main focus of this work is the development of new processes, which will be able to improve fatigue resistance, to test effectively and reliably Nitinol for surface inclusions, alter surface in the direction of improved bio- and haemocompatibility, and simultaneously sterilize Nitinol biomaterial. Shabalovkaya et al. devoted several works to study Nitinol

[13-16] concerning also its shape memory and superelastic effects. The tendency to fracture is the Achilles' heel of Nitinol vascular implantable devices [17-21] as well as rotary instrumentation used in dentistry [8, 17]. The fractures were reported for Nitinol peripheral stents [11, 18] as well as for vena cava filters IVC [19-21].

It is very important to find the best possible way to finish Nitinol implantable devices after all production steps (machining, drawing, shape seating and aging, and oxide removal, including sterilization), and establish one binding protocol. Currently, electropolishing process [22], followed by sterilization [7], is the basic standard of finishing Nitinol implantable devices such as: stents, heart frame valves, inferior vena cava filters IVC, etc. According to a new enhanced theory of electropolishing, published recently by Rokicki and Hryniewicz [23], the indispensability of viscous layer, which is postulated in almost all electropolishing theories, seems to be questionable.

Our works on electrodissolution during the study of electropolishing processes have revealed that not all of them can be explained by a diffusion theory [23]. It appears the diffusion theory contradicts the experimental results, so a possible explanation is that not all electrodissolution processes are governed by diffusional principles, especially when they are run under oxygen evolution regime, above *plateau* level [23]. On the other hand, when magnetoelectropolishing process is performed below oxygen evolution regime and under constant potential, the Lorenz force thins diffusion layer, the current increases and more material is dissolved. In such a case, the magnetoelectropolishing process obeys diffusional theory of electrodissolution [24]. During magnetoelectropolishing some oxygen molecules are attracted by the existence of magnetic fields and adsorb dissociatively on the cyclically oxidized surfaces. The dissociatively adsorbed oxygen must be responsible for the decrease of current density and consequently for the rate of dissolution of magnetoelectropolished materials.

One of the most widely used electrolytes for electropolishing Nitinol, which gives satisfactory, shiny finish, is the solution of H_2SO_4 in CH_3OH [24]. This electrolyte is used in temperature between 0-10 °C. Two different kinds of electrolytes were used in the study of bare Nitinol surfaces by Shabolovskaya [25]. The electrolyte to electropolish austenitic Nitinol consisted of 10% perchloric and 90% acetic acid mixture and was used under constant 20 V potential at room temperature. The martensitic Nitinol was electropolished in 70% methanol and 30% nitric acid mixture at −45 °C. Both electropolished surfaces showed satisfactory finish. Simka et al. [22] in his electropolishing-passivation studies of Nitinol used electrolyte composed of sulfuric acid/hydrofluoric acid/ethylene glycol. Smoothing and brightening of Nitinol surfaces were achieved.

To some electrolytes for electropolishing Nitinol, sodium hypochlorite (NaClO) is added. This NaClO component has a broad spectrum of antimicrobial activity, however, it is not able to destroy endospores and therefore cannot be classified as sterilization agent. Instead, it is classified as disinfectant. It is widely used in dentistry to clean and decontaminate endodontic rotary files used in root canal procedures. As almost all rotary endodontic files are made of Nitinol, it is very important to study the influence of NaClO on this alloy. It has to be mentioned that NaClO is used not only as cleaning and disinfecting agent but also as lubricant and irrigation agents during the procedure [3, 10].

Presently it is not possible to produce totally inclusions-free Nitinol [26-35]. However, the most sophisticated production methods are decreasing Nitinol inclusions content and more refined Nitinol products are reaching the medical devices market, e.g. Euroflex extra low-

inclusion Nitinol [2, 33]. Before implantation, Nitinol medical devices undergo a variety of chemical and electrochemical finishing treatments. They are acid etched, anodized, plasma discharged treated, etc. However, a big part of Nitinol implantable devices undergo electropolishing processes. According to Shabalovskaya et al. [14], chemical etching leaves surface free of inclusions except for some insoluble titanium dioxide particles. However, electropolishing process which results in smoother and passive surface, leaves more chemically different particles on the surface. This was confirmed experimentally [3] during investigating electropolished Nitinol wire for intermetallic inclusions using 6% NaClO testing solution.

Another highly important problem of Nitinol wires, tubes and parts, instruments, needles, files and reamers, is their fatigue resistance to fracture [7-12, 17-21, 27-29, 33, 36]. Specifically endodontic files which rotate, undergo repeated cycles of tension and compression, may result in crack initiation and eventually in fracture. A very comprehensive review of mechanical fatigue and fracture of Nitinol which considered almost every aspect of this phenomenon (phase transformation, transformation temperature, oxide and carbides inclusions, Ni and Ti rich precipitates, levels of strains, etc.) has been recently published by Robertson et al. [11].

This work is aiming at the study of fatigue resistance of Nitinol parts treated by the electrochemical processes, with the most important process of magnetoelectropolishing (MEP). Further on, chemo-physical properties of the oxide which cover Nitinol parts, surgical tools and implants, are also investigated to reveal the critical importance of the surface film and composition of this layer affecting such properties like fatigue resistance and biocompatibility. Additionally, a simple chemical test for detecting intermetallic surface inclusions, which are the main source of nickel leaching and the initiation of fatigue cracks of surgical tools and implanted Nitinol medical devices, is also developed.

2. METHOD

The magnetoelectropolishing (MEP) was performed using Lambda-EMS 40V-25A direct current power supply. The electrolytic cell was assembled with stainless steel mesh cathode positioned around the inner wall of the glass beaker, which was positioned inside four ring ceramic magnets stacked together (see **Fig. 1**). The same set-up was used for electropolishing (EP) and magnetoelectropolishing (MEP) processes varying with the use of magnets in the case of magnetoelectropolishing. The proprietary electrolyte consisted of a mixture of organic acid and alcohol, and the MEP process was performed in a temperature of 37.5 °C.

Four types of specimens, the Nitinol surgical needles, were prepared for fatigue testing:

- Laser cut needles with blue oxide without further finish, as-received (AR)
- Needles electropolished on the *plateau* level of polarization curve, without oxygen evolution (EP)
- Electropolished in transpassive region of polarization curve, under oxygen evolution (EP+)
- Magnetoelectropolished in transpassive region of polarization curve, with oxygen evolution (MEP).

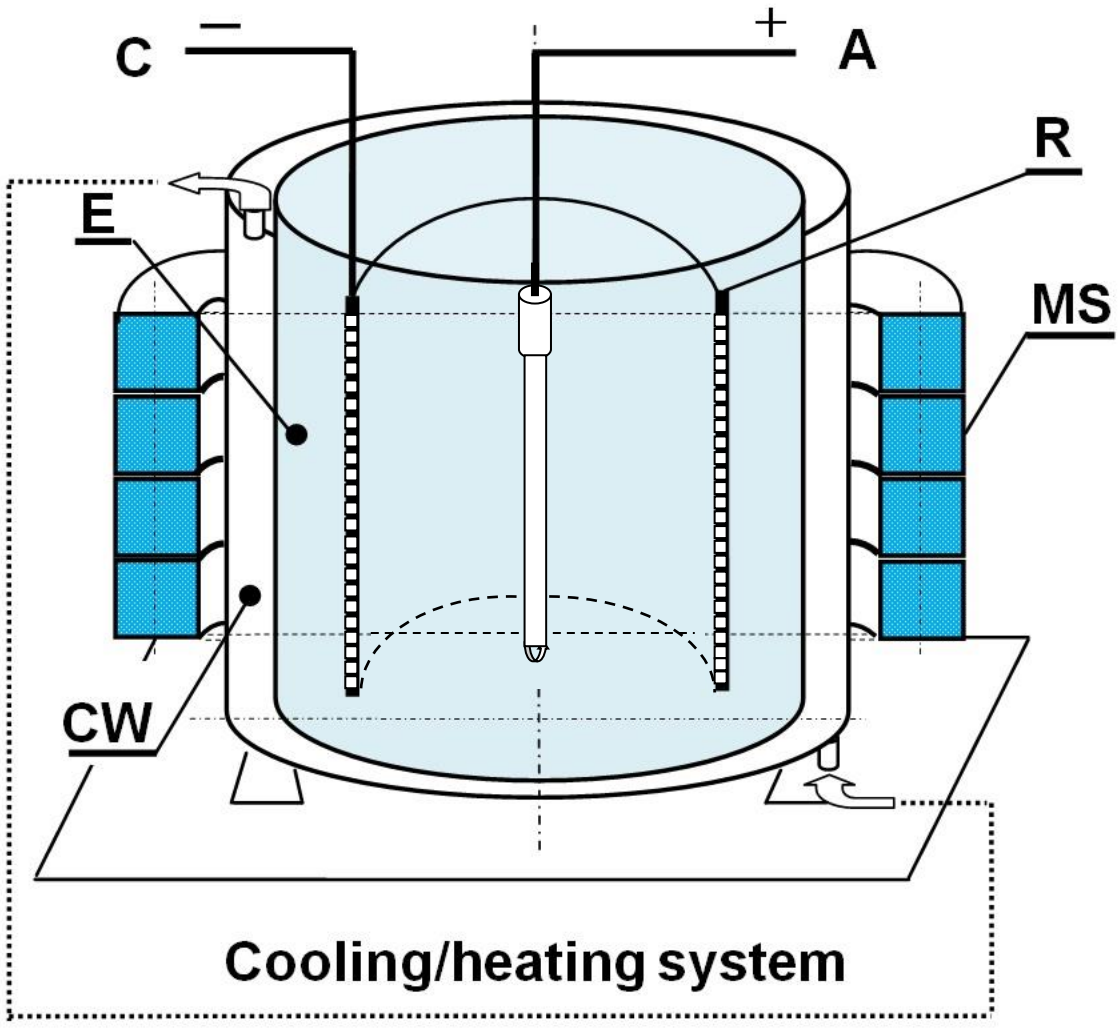


Fig. 1. Schematic view of the set-up used for magnetoelectropolishing MEP with the sample-Nitinol needle connected to anode A: C – cathode connection, R – cylindrical perforated cathode, MS – magnetic rings, E – electrolyte, CW – cooling water

Electrical discharge machining EDM or laser (AR) cut needles were included as a reference in the experiments on bending cycles testing to compare the fatigue resistance improvement after each of the electropolishing treatment. Cyclic fatigue testing of Nitinol needles (**Fig. 2a**), used during arthroscopic meniscus repair surgery, was carried out using the Mark 10 ESM 301 tester [36], with a custom-made needle guide (**Fig. 2b**).

The test was designed by a manufacturer, which rolled out this product on an international orthopaedic market. The testing conditions imitated actual conditions, which occur during non-invasive meniscus surgery. The Nitinol needle consists of two parts welded together. The flat part of the needle (Fig. 2a) is topped off with a hook, whose threads suture undergo double bending during the surgery. This part of the needle is 50 mm long, 1.42 mm wide and 0.29 mm thick. During the test, the needle bends 90˚ in one direction and further 70˚ in opposite. The second part of the needle consists of a 205 mm rod of 1.53 mm diameter,

which pushes and pulls the needle during surgery. The tested needles were pushed and pulled from a custom-made guide with 178 mm/min speed till fracture. Fig. 2b shows a schematic diagram of a test site for the fatigue needle testing.

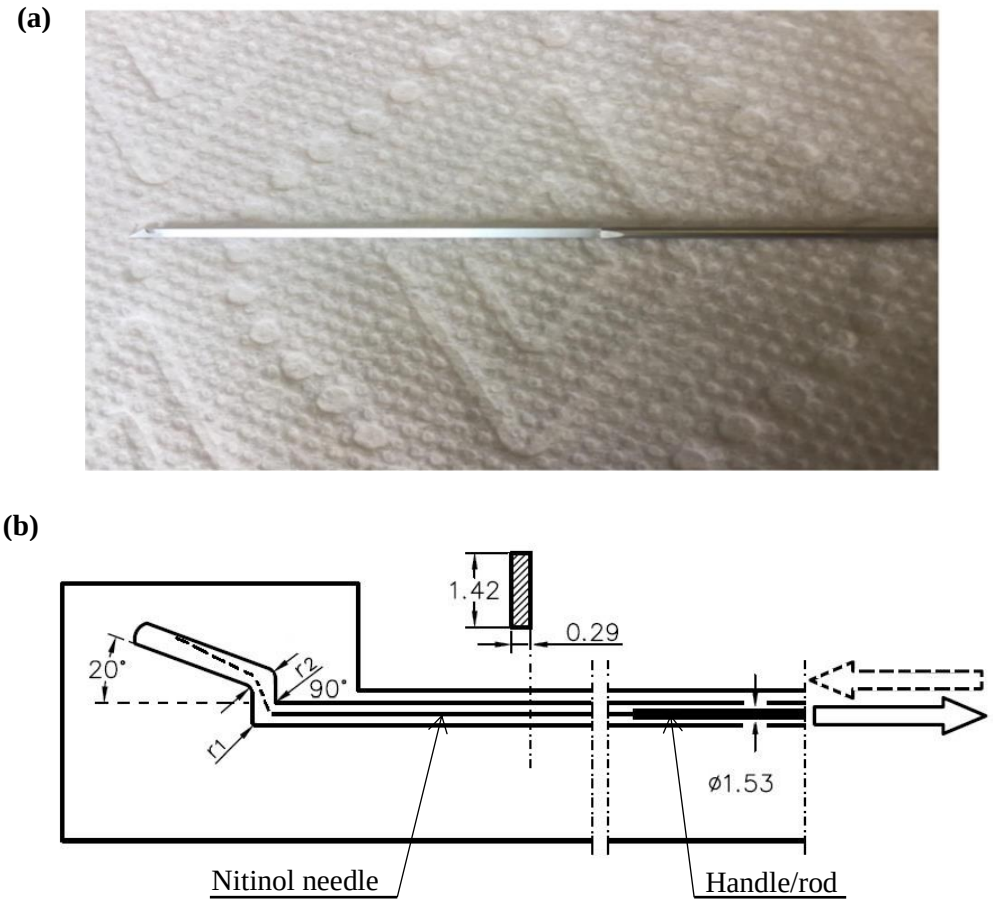


Fig. 2. Nitinol needle **(a)** and the scheme of test site for the needle fatigue testing **(b)**: view from above

The following studies were carried out to clarify the Nitinol fatigue testing results. They are Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS) studies, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), and X-ray Diffraction (XRD) studies.

XPS study of surface chemistry was performed using PHI QUAUTERA SCANING XPS MICROPROBE (Physical Electronics a Division of ULVAC-PHI).

XRD study was done using ARL EQUINOX 100 X-ray Diffractometer (Thermo Fisher Scientific).

Besides, inclusions were observed during studies. Detection of surface inclusions was performed using 6% NaClO in room temperature. Nitinol samples were submerged in 6% NaClO solution in glass beakers and visually observed for any traces of black flocculant of

nickel hydroxide for 15 minutes; those with inclusions were rejected and not underwent for fatigue testing.

3. RESULTS

3. 1. Bending tests

Table 1 shows the double bending test results of Nitinol needles finished by four different processes, being tested five times each. The mean (Avg) and standard deviation (StDev) are presented in the Table 1.

Table 1. Fatigue test results of Nitinol suture needle pusher (done for n = 5)

Specimen	Test 1	Test 2	Test 3	Test 4	Test 5	Avg	StDev
Laser cut needle with blue oxide without further finish (AR)	**30**	**31**	**32**	**28**	**29**	**30**	**1.4**
Electropolished on the plateau region of polarization curve without oxygen evolution (EP)	**37**	**29**	**47**	**36**	**52**	**40**	**8.2**
Electropolished in transpassive region of polarization curve with oxygen evolution (EP+)	**53**	**63**	**44**	**43**	**57**	**52**	**10.1**
Magnetolectropolished in transpassive region of polarization curve with oxygen evolution (MEP)	**220**	**97**	**179**	**109**	**111**	***143**	**46.5**

*143 – apparent average number of cycles

The test results clearly show (Table 1) that magnetoelectropolishing (MEP) process is able to fundamentally modify Nitinol's mechanical properties in the way that the biomaterial part reveals much higher fatigue resistance during its methodic bending. The average apparent number of test cycles until fracture for the magnetoelectropolished needles is almost three times greater than that for the electropolished one. Nonetheless, the MEP finish poses the highest standard deviation among other finishes.

The maximum bending cycles number reached for MEP finish (220) is more than double the minimum one (97), (see Table 1). One may note that the big spread is almost five times larger than that of the spread for the two other electropolishing finishes (EP and EP+). For this reason, it would be more appropriate to divide the MEP bending results into two subgroups. One subgroup includes three bending results (97, 109, 111-bending cycles till fracture) and the second one consists of two bending results (220, 179-bending cycles till fracture). The big spread in the MEP group can be explained by the size of the surface intermetallic inclusions and their displacement at the sample surface. It is well known that

larger surface inclusions are more likely to speed up the initiation of fatigue cracks more than smaller ones [41].

This phenomenon was most probably responsible for faster fracture in the subgroup one, of MEP parts. Taking into account the poor reproducibility of Nitinol products [13-15, 35, 36], the second subgroup of tested needles most likely had tinier sized surface inclusions. However, the lowest number of bending cycles until fracture in the MEP group is almost two times higher than the ones in both EP groups. This can only be explained by differences in properties of titanium oxide created by MEP and EP processes. MEP creates more stoichiometric, more homogeneous titanium oxide, which poses better elasticity and by that improves fatigue resistance during the bending test. The big spread can be explained by the intermetallic inclusions phenomenon. Somehow the needles with a lesser number of bending cycles until fracture most probably had the surface intermetallic inclusions, which resided on the surface and were either not totally dissolved or were revealed during the MEP process. The large spread of numbers of bending cycles irrefutably validate the proposed 6% NaClO test for the detection of surface intermetallic inclusions, which allows to discard faulty Nitinol parts. It also has to be pointed out that the needles electropolished in the transpassive region withstand more numbers of test cycles before fracture than needles electropolished in the standard way, namely in the *plateau* region, below oxygen evolution regime.

Sodium hypochlorite (NaClO) has broad spectrum of antimicrobial activity, however, it is not able to destroy endospores and therefore cannot be classified as sterilization agent. Instead, it is classified as disinfectant. It is widely used as water and laundry disinfectant, cleaner of environmental surfaces and is also used in dentistry to clean and decontaminate endodontic rotary files used in root canal procedures. As almost all rotary endodontic files are made of nitinol, it is very important to research the influence of NaClO on Nitinol. It has to be mentioned that NaClO is used not only as cleaning and disinfecting agent but also as lubricant and irrigation agents during the procedure.

However, the literature regarding the influence of NaClO on corrosion and fatigue resistance of Nitinol rotary files is very controversial and full of discrepancies. Concerning the effect of externally applied magnetic field during magnetoelectropolishing, resulting in so high increase in bending cycles during testing Nitinol suture needle pushers, one should refer to the higher mentioned inconsistency in the diffusion theory. A possible explanation is that not all electrodissolution processes are governed by diffusional principles [20], especially when they are run under oxygen evolution regime.

On the other hand, when magnetoelectropolishing process is performed below the oxygen evolution level, under constant potential, the Lorenz force thins diffusion layer, the current increases and more material is dissolved. In such a case, the magnetoelectropolishing process obeys diffusional theory of electrodissolution. Although the origin of the two-way influence of externally applied magnetic fields on magnetoelectropolishing processes is not fully understood and requires a good deal of further research and clarification, one possible explanation of the effect can lie in the properties of the oxygen molecule and its behaviour in a magnetic field.

The oxygen which is adsorbed on the surface by dissociation seems to be responsible for the decrease of current density and consequently for the rate of dissolution of magnetoelectropolished materials.

3. 2. Surface roughness

Surface roughness measured by AFM (**Table 2**) showed the same trend in roughness decrease EP > MEP. Almost the same Ra parameters for electropolished Nitinol surfaces for the same scan sizes were reported by Summy et al. [35], which were Ra = 15 and Ra = 8 nm for 6 × 6 and 3 × 3 mm scan, respectively. The decreased surface roughness after magnetoelectropolishing process was confirmed earlier using other measuring techniques [3, 24-26], also on other metals and alloys.

Table 2. Roughness of EP and MEP Nitinol surfaces measured by AFM

	6 × 6 mm scan		3 × 3 mm scan	
Sample treated by	Ra, nm	Rmax, nm	Ra, nm	Rmax, nm
EP	12.6	219	9.9	125
MEP	5.1	109	3.6	58

3. 3. SEM and EDS studies

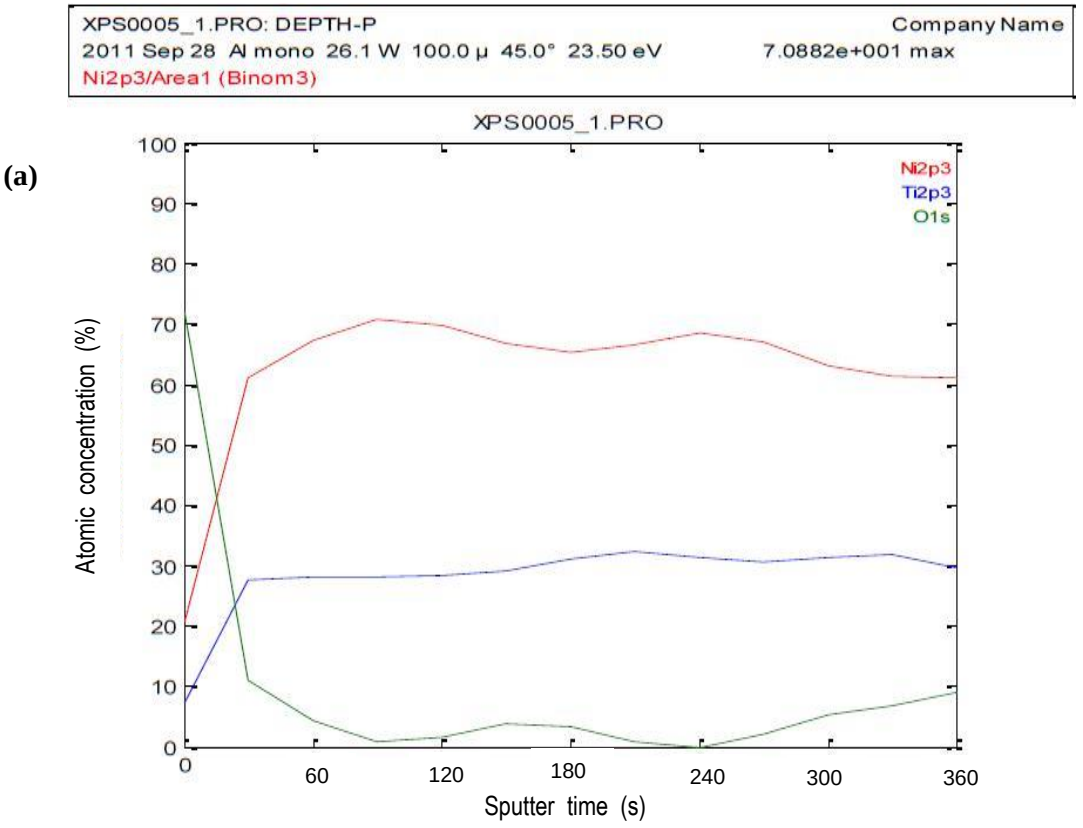
It is well known that during roughness investigations by SEM, a difference in surface pattern of EP and MEP surface, with wavy patterns, can be easily revealed [22, 24-26]. A similar unexplained wavy pattern of electropolished nitinol surface was earlier reported by Summy et al. [36]. The depth profiles of nickel are very similar for both samples. However, titanium shows changes from the beginning and through sputtering time. From the beginning of analysis percentage content of titanium in oxide film is higher for MEP sample than for EP one and amounts to ~ 16% and ~ 2%, respectively. After 6 minutes of sputtering, titanium content reaches ~32% for MEP and only ~20% for EP sample. This higher content of titanium in passive oxide layer of MEP samples was also confirmed by EDS for three consecutive dispersive energies: 10, 15, and 20 kV. The atomic Ti concentrations were 1.9, 9.0, and 15.0 – after EP, and 2.2, 10.2, and 15.8 – after MEP, respectively.

3. 4. XPS study of electrochemically treated Nitinol surfaces

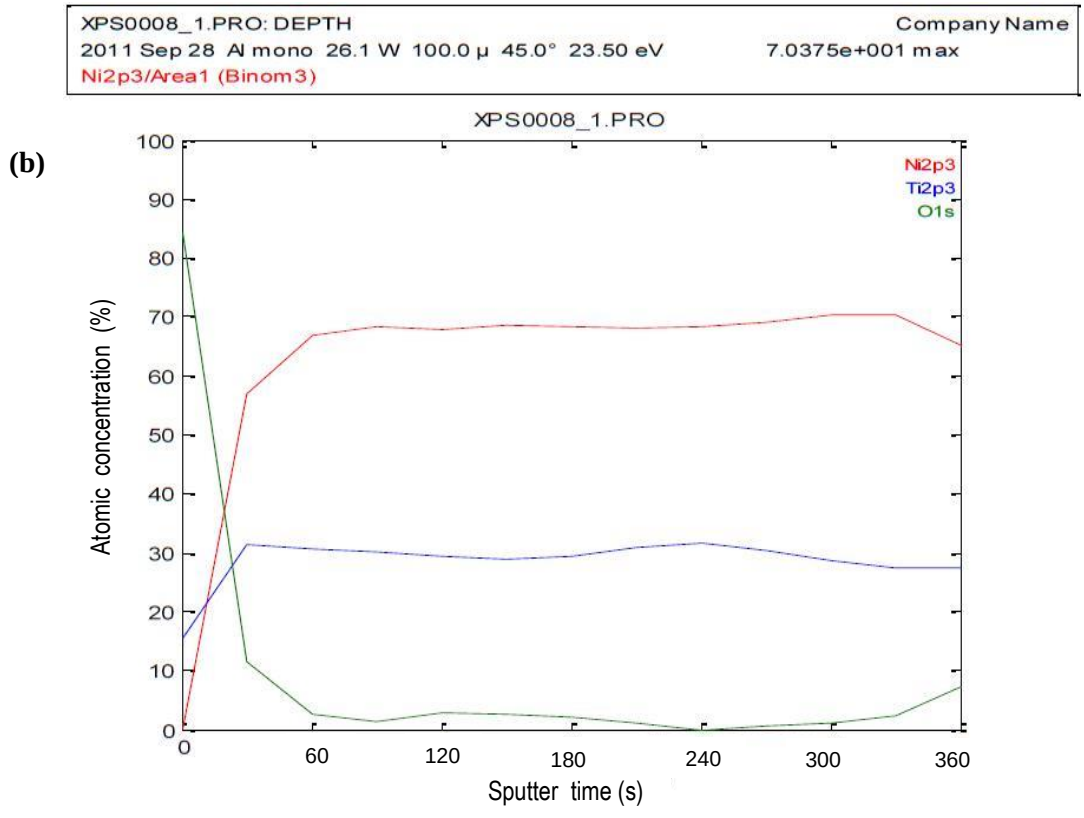
The electrochemically processed Nitinol samples after consecutive treatments by:

1) electropolishing EP
2) magnetoelectropolishing MEP
3) electropolishing EP + 6% NaClO treated
4) magnetoelectropolishing MEP + 6% NaClO treated

where undergoing X-ray photoelectron spectroscopy (XPS) analysis for their surface layer chemical composition studies. Detailed method describing the XPS analysis using monochromatic Al Kα X-ray radiation, including sputter depth profiles and the sputter etching rate, was given elsewhere [26].

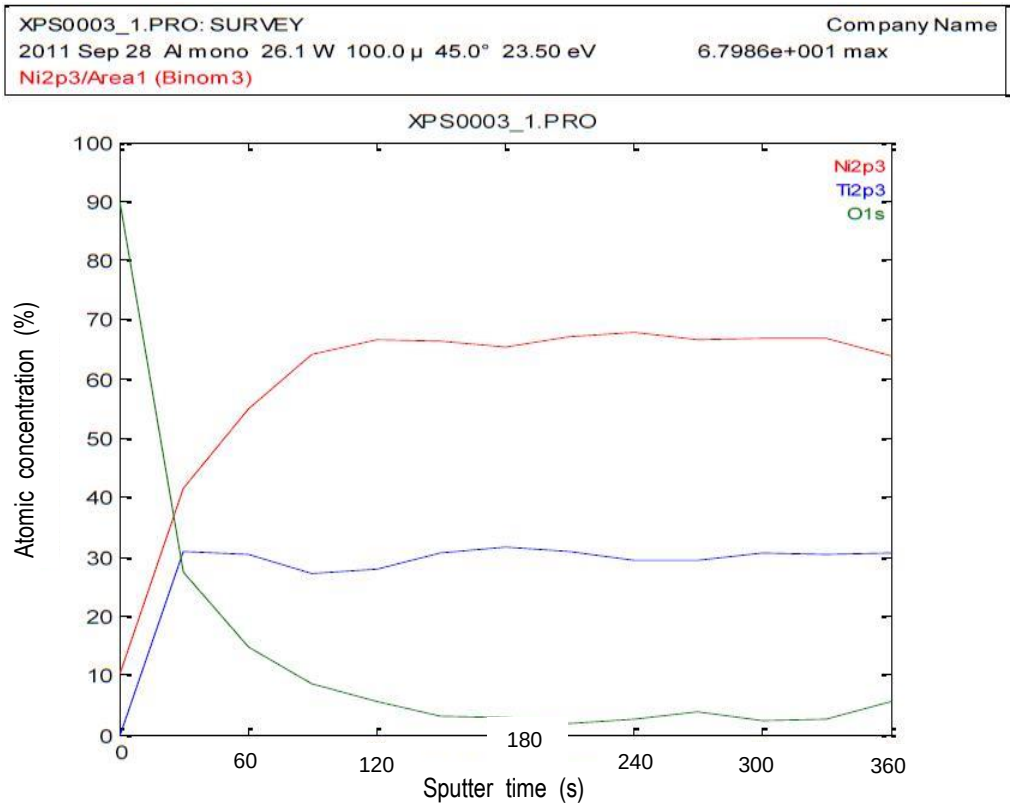


(a)

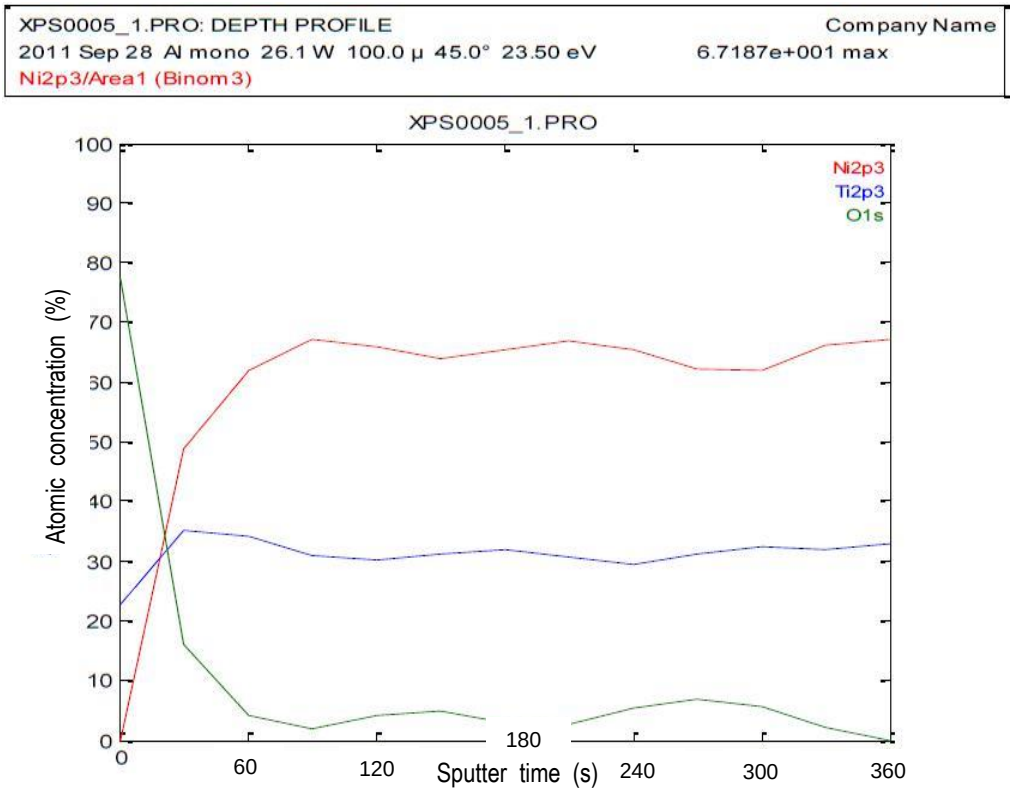


(b)

Fig. 3. XPS depth profiles of: **(a)** EP Nitinol surface, and **(b)** MEP Nitinol surface



(a)



(b)

Fig. 4. XPS depth profiles of: **(a)** EP + 6% NaClO Nitinol surface, and **(b)** MEP + 6% NaClO Nitinol surface

The oxygen concentration appears to be the highest on the surface and then sharply diminishes during first 30 seconds of sputtering time. The Ni content and Ti profiles indicate the lowest concentration near surface and then return to steady state of bulk of the alloy. In the case of MEP and MEP + 6% NaClO treated samples, Ni in any form was not detected in the outermost layer of samples (Fig. 3b and Fig. 4b). The amount of titanium after MEP + 6% NaClO treatment on Nitinol surface is also meaningful (see Fig. 4b). The XPS studies clearly show that electropolishing treatment without the magnetic field leaves much worse the Nitinol surface concerning much higher amount of nickel both without (EP), and with additional 6% NaClO treatments (see Figures 3a and 4a).

3. 5. XRD study

The same characteristics of austenitic patterns of NiTi SMA (shape memory alloy) are found in electropolished as well magnetoelectropolished samples after processes performed in transpassive region of polarization curve under oxygen evolution regime (**Fig. 5**). Both samples show characteristic peaks for austenite phase Nitinol (42,31˚, 61,88˚, 77,51˚); they are marked by respective Miller indices (110), (200) and (211).

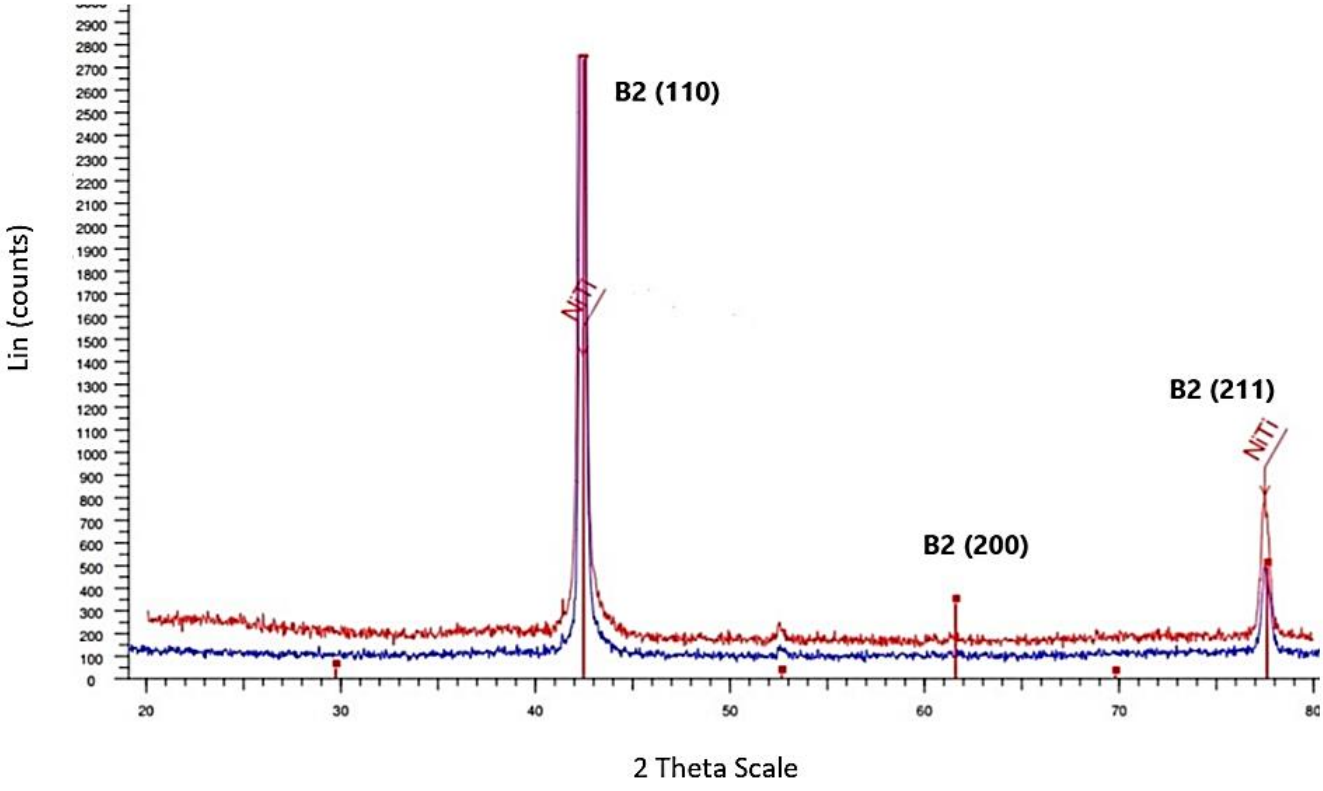


Fig. 5. XRD analysis of austenitic Nitinol after EP (blue_lower) and MEP (red_higher)

The XRD graphs of EP and MEP samples (Fig. 5) are mirror images of each other. This finding shows that EP and MEP processes performed in a transpassive region do not change bulk properties of material. But fatigue testing results of both finished samples show very big

differences in their properties. The XRD penetrates through the bulk of the oxide crystals up to about 10^5 nm and that depth of penetration goes far beyond the oxide thickness of EP as well as MEP nitinol samples, which are about 6 and 4.5 nm, correspondingly. From this, only one conclusion can be reached, namely the difference in fatigue resistance is caused by oxide properties themselves. This fact means that, to avoid intense signal from the substrate and get stronger signal from the film itself, a fixed grazing angle of incidence with Grazing Incidence Diffraction (GID) technique is necessary to be used next to support the present findings. Grazing Incidence Diffraction, also ideal for determining the morphology of novel materials, may be helpful to reveal any differences in oxide structure between these – EP and MEP – two layers.

4. DISCUSSION

The studies have shown that Nitinol biomaterial devices can be highly improved concerning their mechanical fatigue resistance, decrease in surface roughness, nickel removal from the surface, corrosion resistance and pre-elimination of parts with oxide inclusions which are likely to initiate fatigue micro-cracks and cracks. To reveal this improvement, a fatigue testing was carried out (**Fig. 6**) supported by AFM surface roughness studies, SEM with EDS, XPS, and XRD studies. This way the magnetoelectropolished Nitinol parts in transpassive region of polarization curve appeared to possess features of the best biocompatibility (no nickel on the surface). Fig. 6a presents average number of cycles (out of 5 measurements) until fracture, whereas Fig. 6b shows extreme number of sample bending until fracture.

A good deal of work was devoted to the study of electropolishing processes [3, 4, 14, 20, 24-26], many of them recently with the use of externally applied magnetic field [3, 26-31]. During magnetoelectropolishing of Nitinol under an oxygen evolution regime, in addition to electrolytic smoothing and reduction of nickel content in the passive protective layer, the Nitinol surface outermost oxide layer and consecutive deeper underlayers are enriched in oxygen without any significant thickness changes. These additional oxygen ions are incorporated into the profile of the passive layer and are responsible for bridging and saturating the oxide lattice defects making the passive film more stoichiometric and homogeneous [22, 24-27].

The more perfect homogeneous oxides with lower lattice defects consequently improve fatigue resistance of Nitinol medical implantable devices and instruments by improved elasticity of titanium oxide crystals covering the surface, which slow down the crack initiation phenomenon. Our additional experiments were carried out on the 0.7 mm thick Nitinol surgical blades after EP and MEP to present their mechanical behavior. The bending tests had shown that electropolished part had fractured at about 120° and the magnetoelectropolished one withstood full 180° bending. It appears that much thicker Nitinol surgical blades (0.7 mm in comparison with presented above 0.29 mm thick Nitinol needle) revealed superiority of magnetoelectropolished part under bending test.

The oxygen spectra of all four samples show the characteristic double peak configuration [4] which was earlier reported by Shabalovskaya et al. [14-16]. Moreover, the XPS of combined oxygen signals show oxidation enhancement of EP and MEP samples which underwent 6% NaClO treatment compared to non-NaClO treated counterparts; the

obtained combined intensity of oxygen signals to the depth of penetration (of about 13 nm, c/s) equal after: (1) EP – 7,800, (2) MEP – 8,800, (3) EP + 6% NaClO – 10,000, and (4) MEP + 6% NaClO – 11,400. These results clearly display consecutive increase of oxygen content, with the highest amount of oxygen noted in the last case.

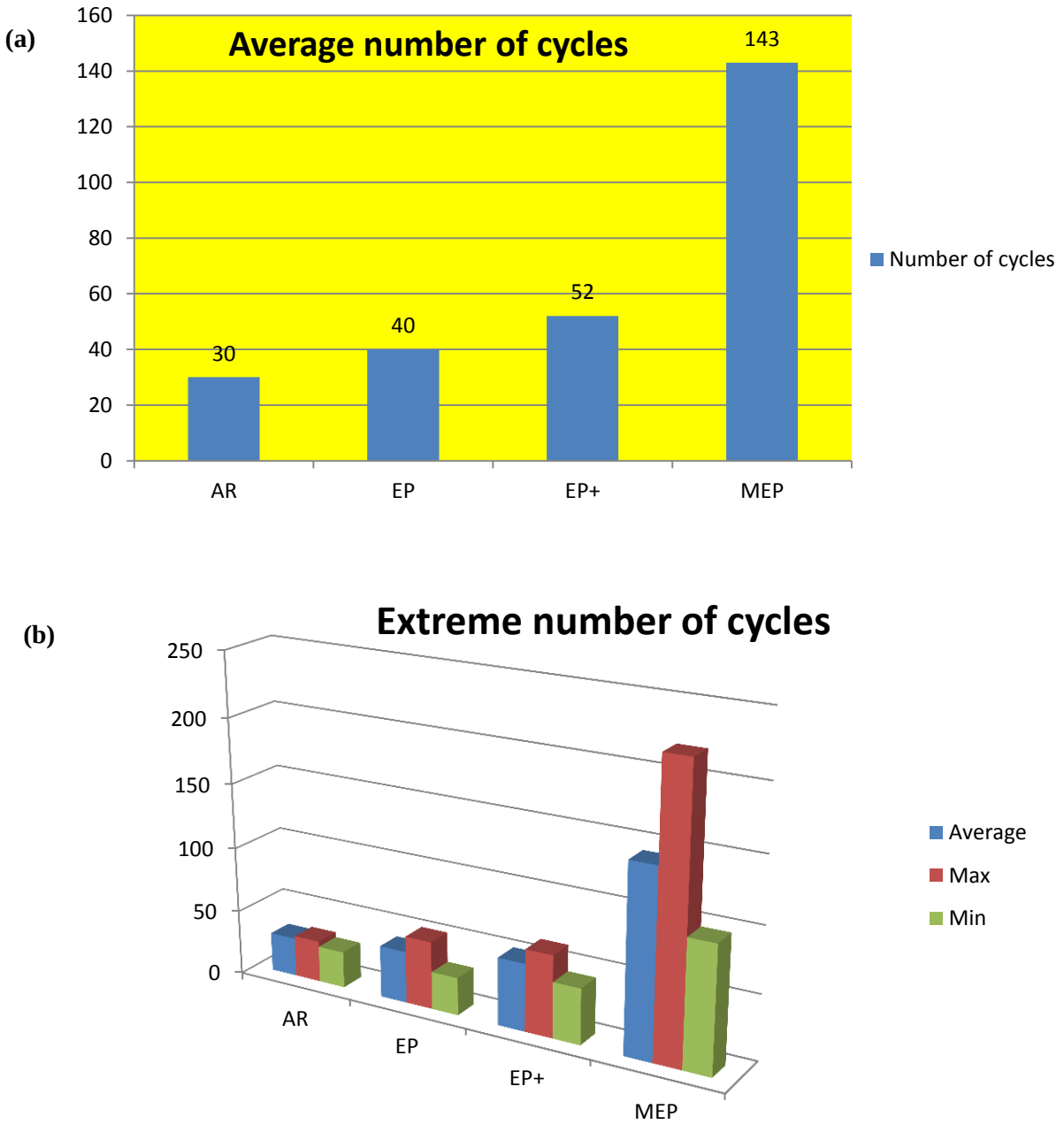


Fig. 6. Number of bending cycles of Nitinol needle until fracture: **(a)** average, **(b)** extreme values (for 1 push/pull bending cycle, see Fig. 2)

It should be mentioned that electrolytically introduced oxygen into the passive layer does not enrich the metal-oxide interface in metallic nickel and its compound as thermal oxidation processes do and by this eliminates another possible source of crack initiation. When the electropolishing at the conditions of oxygen evolution is performed in a magnetic field (magnetoelectropolishing), this oxygen behavior in the magnetic field is characteristic with specific reaction. Due to a magnetic field, more oxygen will adsorb on the Nitinol surface and more oxygen ions will be tunneled toward the Nitinol surface through vacant and dislocation sites. It should be mentioned that simultaneously more nickel ions will be leaving the oxide layer and entering the electrolyte due to its ferromagnetic properties. The oxide layer will become composed almost entirely of titanium dioxide (TiO_2). The highest oxygen concentration will lead to a higher extent of saturation and bridge lattice defects making the passive film more homogeneous and elastic with increased fatigue resistance.

Corrosion studies of electrochemically treated Nitinol samples were performed in Ringer's solution and presented earlier [24-27] with the resistance comparison results showing the range of improvement after MEP [24]. Specifically the meaningful re-passivation phenomenon observed on MEP curve after a particulate detachment was to prove of prevailing function of the magnetic field in magnetoelectropolishing [24].

The once overlooked issue of nitinol intermetallic inclusions, which create problems for nitinol implantable devices such as fractures, corrosion (especially pitting corrosion), nickel leaching as well as whole particles release to the body environment, has received more attention recently. Presently it is not possible to produce totally inclusions-free nitinol. However, the most sophisticated production methods are decreasing nitinol inclusions content and more refined nitinol products are reaching the medical devices market, e.g. Euroflex extra low-inclusion nitinol.

One more issue which has not been undertaken in the present study is the problem of de-hydrogenation. The hydrogen content may be effectively studied by Secondary Ion Mass Spectroscopy (SIMS) and/or Glow Discharge Optical Emission Spectrometry (GDOES). The authors' recent studies on magnetoelectropolishing of niobium [44-46] show that this process leaves the niobium surface layer almost completely free from hydrogen contamination. Specifically the Glow Discharge Optical Emission Spectrometry (GDOES) analysis of niobium de-hydrogenation during MEP indicated that in the surface film there was only about 9% of hydrogen left in comparison with that one measured in AR (as-received) sample [37]. Even if the hydrogen content in electropolished (EP) Nb surface decreased of about 30%, so in the magnetoelectropolished (MEP) surface layer it dropped down of over 90%. Such results mean also a revolutionary change in the surface film structure and surely capable to affect the mechanical behavior of a part after MEP [38]. In view of the fatigue results after magnetoelectropolishing (MEP) presented above, one should assume a similar reduction in hydrogenation of Nitinol parts as well.

Therefore one should add that some more other than the higher mentioned techniques are necessary to be used in the near future to develop and confirm the study results. They are SIMS, GDOES, and GID which will be helpful to acquire data serving for detailed explanation of the outcomes and reason for outstanding results of fatigue resistance of Nitinol after magnetoelectropolishing.

5. CONCLUSIONS

Based on the study results, concerning fatigue resistance testing as well as post-treatment investigation, some essential conclusions may be formulated:

1) The development of electropolishing processes (EP+ and MEP) was undertaken by the authors as the answer to the two main problems of presently available Nitinol for the production of medical implantable devices, namely: fatigue resistance and haemocompatibility. The haemocompatibility of Nitinol is generally improved by nickel removal from the surface film in view of avoiding its leaching to surrounding tissue upon implantation. The second problem which creates a lot of complications for an implantable Nitinol medical device is its tendency to fracture after implantation which in most cases is initiated by surface intermetallic inclusions.
2) The results of this work indicate that magnetoelectropolishing process alone is able to improve haemocompatibility and fatigue resistance of Nitinol implantable medical devices or can work in tandem with NaClO test-procedure to the greater extent of the benefits.
3) The following further conclusions are obtained from this study:
   a) The fatigue resistance (number of cycles till fracture) of MEP-treated Nitinol surgical devices showed almost three-fold improvement compared with EP ones (143, and 52, respectively).
   b) MEP treatment minimizes nickel leaching from Nitinol surface by the enhanced removal of nickel from outermost layer of passive film by utilizing selective dissolution caused by application of external magnetic field.
   c) The passive layer on MEP Nitinol consists totally of TiO_2 and its sub-layer is enriched in O_2 when compared to EP surface.
   d) The MEP surface shows improved roughness and decreased wettability compared to EP surface.
   e) The 6% NaClO test is able to detect surface intermetallic inclusions which are the main sites for crack initiation leading to fracture of raw, oxidized, mechanically polished, EP and MEP Nitinol surfaces upon their presence.
   f) The present work, first of all, shows the way of improving Nitinol fatigue resistance. MEP process is able to improve fatigue resistance of Nitinol to the great extent (at least three-fold).

To sum up, the study results clearly show that Nitinol implantable medical devices and surgical tools made of that material can be easily improved in the direction of enhanced haemocompatibility and fatigue resistance by applying the novel electrochemical finishing treatment namely magnetoelectropolishing followed by 6% NaClO test-procedure.

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