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Magnetoelectropolished Titanium Biomaterial

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1. Introduction

The high standard and bio-electrochemical stability of any metallic biomaterial components are the main conditions for their safe implantation into human body. The most critically indispensable properties for metallic biomaterials are their corrosion resistance, inertness, low toxicity, and durability. The work aims at analyzing the titanium biomaterial characterization after electrolytic polishing in a magnetic field, named as the magnetoelectropolishing (MEP), in comparison with the material finish after a conventional electropolishing (EP).

Titanium and titanium alloys gradually became the main biomedical materials used presently in orthopaedic applications. The leaching of metallic ions such as nickel during the corrosion process from other biomaterials such as: 316L stainless steel, L-605 cobalt-chromium alloy, or Nitinol, has caused considerable concerns due to the allergies, inflammations, etc. It appears to be non existent when CP titanium is employed. Titanium is also insensitive to oxygen concentration and by this titanium ions release by this mechanism is not applicable in this case. Also it is well known that when titanium is exposed to body fluids, its surface undergoes spontaneous modification by Ca^{2+} and PO_4^{3-} ions and prolong exposure leads to formation of hydroxyapatite layer, which is indispensable to bone-implant osseointegration.

High quality metal alloys of titanium are commonly used for orthopaedic prostheses as bone plates, nails, screws, etc. Fortunately, the oxides and hydroxides of titanium have extremely low solubilities – so a passive oxide film readily and spontaneously forms over the titanium's surface. In spite of its very high corrosion resistance the spontaneously formed oxide film consists of some inclusion and discontinuity spots, which can cause the problems in integration at the bone-implant interface. To overcome these problems, several surface treatments are employed: chemical etching, plasma treatment, ion implantation, electrochemical or wet chemical hydroxyapatite precipitation following either hydrothermal treatment or sintering, anodizing, electropolishing, etc. The electropolishing process seems to be the best way to eliminate these problems. By dissolving the existing imperfect oxide, electropolishing process creates the base for formation the more perfect homogeneous oxide over the base titanium metal. As it was shown in many works, including also previous ours, it is the presence of this oxide film that is responsible for titanium's excellent corrosion resistance, which enables it to be used in surgical applications.

2. Titanium biomaterial characteristics

Titanium and some of its alloys Ti6Al4V, TI6AL7Nb, Nitinol, are classified as biologically inert biomaterials and are commercially used in orthopaedic and dental application. This is a result of their outstanding corrosion resistance and inertness. The inertness of those materials is due to titanium oxide (TiO_2) which spontaneously covers them after exposure to ambient air or water according to the following reactions:

$$Ti + O_2 \rightarrow TiO_2$$

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$$

The stability of TiO_2 can be compromised only by complexing species such as HF or H_2O_2 and can lead to its dissolution. Without those species TiO_2 is thermodynamically stable in the wide range of pH = 2-12 (Schenk, 2001) and by this CP-Ti is totally corrosion resistant in the presence of neutral physiological solutions. In the case of Al-containing alloys (Ti6Al4V, Ti6Al7Nb) acidification of solutions make them more prone to dissolution than CP-Ti (Ruzickova et al., 2005).

In present work our research concentrates on CP Titanium as on precursor of another titanium alloys. Along excellent corrosion resistance, inertness to human body and excellent osseointegration titanium offers more suitable properties for implantable biomaterials. Some of those properties include: fatigue resistance, strength, density, elastic module, etc. The density of around 4.5 $g.cm^{-3}$ makes it almost two times lighter than cobalt-chromium or 316L stainless steel alloys. As pure element CP titanium also excludes possibility of leaching harmful elements which could be detrimental to surrounding tissues as can be in case of 316L stainless steel and Nitinol where possibility of leaching nickel is reality. The biggest disadvantage of CP-Ti is its relatively low wear resistance and by this it should not be used in devices where contact wear is unavoidable as for example modular interface corrosion between Co-Cr heads and Ti stem in total hip replacement prosthesis (Singh &, Dahotre, 2007; Salvati et al., 1995).

2.1 Mechanism of passive film formation and growth

Even that the passive film on titanium is only in nanometers range it creates very protective barrier against biological environment of human body. Its protectiveness depends on several features: morphology, homogeneousness, thickness, kind and quantity of foreign chemicals species incorporated in it. All of those properties of passive film determine the tunneling rate end speed of ions moving through the film as well as its dissolution by surrounding fluids.

According to (Cabrera & Mott, 1948) high field mechanism for oxide film formation and growth theory the main prerequisite is adsorption of oxygen on bare titanium surface which creates oxide monolayer (Fig. 1). The next step is electron tunneling from titanium to monolayer of adsorb oxygen which by adding electrons became electron traps on the outer surface of the oxide. As the number of electron traps increases the potential drop across the films grows. The drop of potential creates the electric field across the passive film which lowers the activation energy necessary for further ions transport though passive film. The oxide on titanium is classified as N-type semiconductor which means that anion transport through film is dominant way of film grow and is due to oxygen ions movement toward titanium metal. The thickening of oxide film increases the activation energy necessary for

further oxygen ions transport and limits further passive film formation. The only way for further grow of passive film in this point is to increase the potential drop across the film which simultaneously increases the electric field.

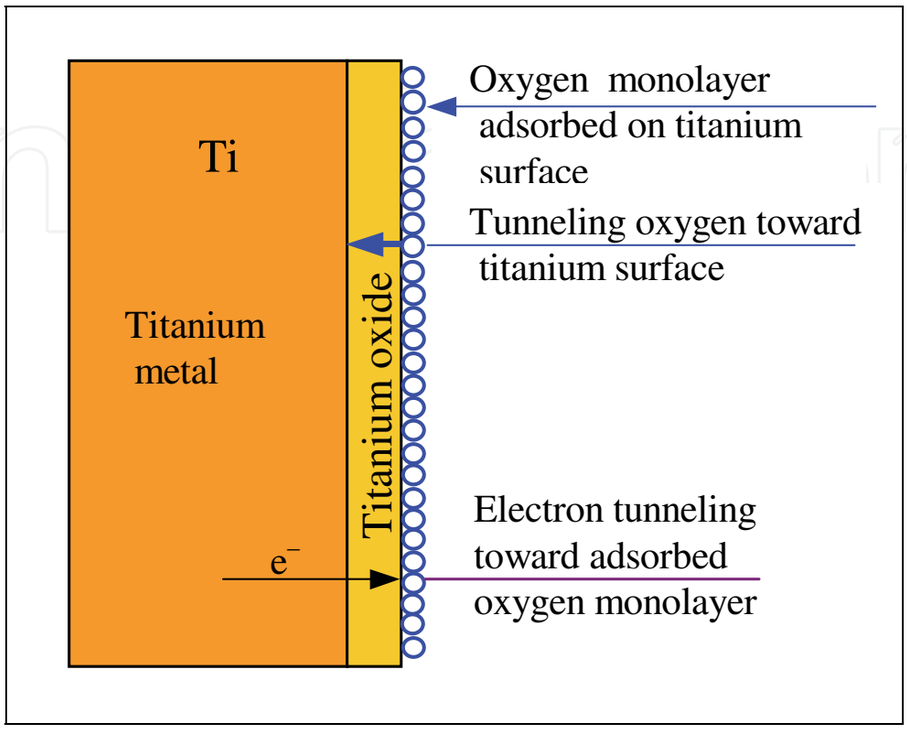


Fig. 1. Oxide growth on titanium.

2.2 Passive film components

The composition of titanium oxides depends on conditions and chemical media in which oxide is created. There are three main forms of titanium oxide which can exist on titanium separately or simultaneously in different proportions. The three main forms of titanium oxides are rutile-tetragonal crystals, anatase – also tetragonal crystals, but of more amorphous form and brookite-orthorombic crystals. To lesser extent Ti_2O_3, Ti_3O_5 and some hydrated oxides can also form on titanium surface. The naturally created oxide is mainly in TiO_2 form, transparent, not visible to eye and less than 10 nanometer thick (Alekseeva, 1964).

2.3 The processes altering the titanium surface

To improve corrosion resistance, biocompatibility, osseointegration, cleanability, overcome galling and seizing problems many processes were invented in last several decades including: acid etching, DC anodizing, AC spark anodizing (Rokicki, 1992), electropolishing, thermal oxidation, conversion coating (fluoride-phosphate), alloying of surface layer with palladium by thermal decomposition, laser irradiation, phothocatalytic treatment, plasma spraying for hydroxyapatite incorporation, and most recently proposed magnetoelectropolishing process (Rokicki, 2009). From all of those processes the most popular is DC anodization. This is very easy to perform not complicated electrochemical

process which gives very attractive colorized finish to titanium in following colour succession: yellow, purple, dark blue, sky blue, greenish, golden-purple (mosaic), violet-greenish (mosaic), and gray. The colour succession is due to thickening of oxide by rising voltage. This process is very often utilized as finish of standard micro-rough CP Ti orthopaedic locking compression plates (yellow colour) because this finish gives very high osseointegration. This is most probably attributed to anatase form of titanium oxide which predominantly covers anodized surface of titanium (Gopal et al., 2003; Simka et al., 2011). Another recently more demanded finish for titanium is electropolished finish. The electropolishing dissolves existing natural oxide with all its imperfections and creates new more corrosion resistant oxide mainly in the form of rutile (Rokicki, 1990) according to following reactions:

1. dissolution and transfer of titanium ions into solution

$$Ti = Ti^{4+} + 4e^-$$

2. evolution of the oxygen from the anode surface

$$4OH^- = O_2 + 2H_2O + 4e^-$$

3. formation of the passive film on the anode surface

$$Ti + 2OH^- = Ti_xO_y + H_2O + 2e^-$$

The oxide created by electropolishing process is very homogeneous with few dislocation sites. The advantage of this oxide over oxides created naturally on mechanically polished or chemically etched titanium surface was shown in experiment performed by the author over two decades ago (Rokicki, 1990). In that experiment two samples of titanium, one electropolished another chemically etched, were anodized to the same colour (golden-yellow which is first colour obtained during anodization). After one year of exposure to ambient atmosphere the colour on chemically etched titanium sample changed colour to purple (thickening of the passive film field). The colour on electropolished sample stays unchanged (and stayed unchanged to this day). Above experiment indicates that oxide on electropolished titanium resists further oxidation by ambient atmosphere. In the case of chemically etched titanium surface the oxide was very unstable and underwent further oxidation by ambient air. This fact supports the Cabrera & Mott (1948) theory of titanium oxide growth by oxygen movement toward titanium surface through existing oxide (Fig. 1).

3. Magnetoelectropolishing of titanium

Magnetoelectropolishing (MEP) appears to be an important and effective process for obtaining modified surface properties (Rokicki, 2009; Hryniewicz et al., 2008; Hryniewicz et al., 2009). In our studies, for comparison the electrolytic polishing was performed both in the absence and in the presence of a magnetic field. The experiments were carried out with the use of wires, commercial endodontic files, and flat samples (plates). For the MEP experiments, a constant external magnetic field below 500 mT was applied to the electropolishing (EP) system by neodymium ring magnets. For both processes, conventional EP and MEP, the same type of an acidic electrolyte was used, which was mixture of sulfuric,

hydrofluoric and nitric acids. We use nitric acid addition to well known H_2SO_4/HF electrolyte composition for electropolishing titanium as a precaution from possibility of hydrogen adsorption during electropolishing. This method was successfully applied by Higuchi & Sato, (2003). Decreased hydrogen concentration in the stainless steel samples after MEP in comparison with EP, and MP ones, was recently reported by Hryniewicz et al., (2011).

The bath was unstirred during the process carried out with absence of externally applied magnetic field. During magnetoelectropolishing the stirring was self imposed by Lorentz Force as a result of interaction of electric and magnetic fields. For comparison, also Ti samples after mechanical polishing using an abrasive paper of the grit size up to 1000 were used.

4. Towards improving the titanium biomaterials

Much attention has been concentrated on improving the properties of titanium biomaterial (Schenk, 2001; Rokicki, 1992; Gopal et al., 2003; Simka et al., 2011; Rokicki, 1990; Hryniewicz et al., 2009; (2) Hryniewicz et al., 2009; Schultz & Watkins, 1998; Virtanen et al., 2008; Buly et al., 1994; La Budde et al., 1994; Burstein et al., 2005; Virtanen & Curty, 2004; Burstein & Souto, 1995; Mickay & Mitton, 1995; Khan et al., 1999; Hanawa et al., 1998; Budzynski et al., 2006; Hayes et al., 2010). Osseointegration of a metallic implant into bone or adaptation in soft tissue involves many complex physiological reactions related both to the material itself and to the living host. It was thus realized that during implantation a hydrated oxide layer grows on titanium, suggested to be due to the metabolic activity at the site of implantation (Virtanen et al., 2008). A prerequisite for clinical success of orthopaedic and dental implants is a strong and long-lasting connection between the implant and bone. Surface roughness has been suggested as one important factor for establishing clinically reliable bone attachments (Buly et al., 1994; La Budde et al., 1994; Burstein et al., 2005; Virtanen & Curty, 2004; Burstein & Souto, 1995). Implant-related factors, mechanical loading, surgical technique, implant site and patient variables influence bonding between implants and bone (Buly et al., 1994). Several authors suggest methods to modify the surface structure of titanium implants, which all may lead to altered chemical and mechanical properties of the metal surface (La Budde et al., 1994; Mickay & Mitton, 1995). Textured implant surfaces can be produced by several methods, all of which provide different characteristics of the biomaterial surface. It is not clear what influence these characteristics have on the bone response after implantation, or to what extent the response depends on geometry and degree of the surface roughness (Khan et al., 1999). Results from in vitro studies suggest a positive correlation between surface roughness and cellular attachment and osteoblast-like cell activity (Duisabeau et al., 2004).

5. Comparison of surface roughness

Definitions of roughness parameters are given in accordance to Polish Standard: PN-EN ISO 4287 (1999),

R – parameter calculated from the roughness profile

Ra – is the arithmetic mean of the sum of roughness profile values

$$Ra = \frac{1}{l}\int_0^l |z(x)|dx \tag{1}$$

where $|z(x)|$ – absolute ordinate value inside the elementary measuring length, with $l = lp$, and lp – elementary length in x direction (on average line) used for identification of unevenesses characterizing profile under evaluation,
R_z – the height of roughness acc. to 10 points as the measure of the range of roughness values in the profile. It is generally determined as the mean of 5 single measuring lengths of the roughness profile it corresponds to the mean peak-to-valley height,
Rt – the total height of the primary roughness profile defined as the difference between height of the highest profile peak and the depth of the lowest profile valley of the respective profile within the evaluation length ln ($l = ln$).
A computerized HOMMEL TESTER T800 system of Hommelwerke GmbH for roughness measurement was used for the study of surface roughness. The comparison of roughness studies results after both conventional electropolishing (EP) and magnetoelectropolishing (MEP) were carried out on the Ti samples.
Surface roughness measurements on CP Ti Grade 2 samples were performed both on wires and plates after standard electropolishing (EP), and magnetoelectropolishing (MEP), with mechanically abrasive polishing (MP) samples serving as a reference. Comparison of the R_z, R_zISO, Rt, and Ra results obtained after MP, EP, and MEP are presented in Fig. 2. Dependent on the treatment proposed, a decreasing surface roughness is observed with MEP roughness being the least (Figs. 2a,b,c).
The maximum height of scale limited surface Sz is the sum of the largest peak height value and the largest pit depth value within a definition area. The arithmetic mean height Sa is the arithmetic mean of the absolute of the height within a definition area

$$Sa = \frac{1}{A}\int_A |z(x,y)|\ dxdy \tag{2}$$

with A being the definition area (Standard ISO 25178-2, 2008).
The interferometric roughness studies were performed on CP Ti Grade 2 strips after MP, EP, and MEP (Fig. 3). The obtained results are even more pronounced with detailed data given in Table 1. Even if Sa surface roughness parameter measured after EP is very low (of 88%) in comparison with Sa after MP, this parameter of Ti sample surface after MEP is still reduced over 12%.
Our previous studies performed on MP, EP, and MEP sample surfaces of different metallic biomaterials indicated decreasing roughness, evaluated both by 2D standard roughness measurements (Ra, R_z, Rt), as well as 3D interferometry measurements (Sa, Sz), (Hryniewicz & Rokosz, 2009) as well as presented in our works elsewhere (Hryniewicz & Rokicki, 2007; (2) Hryniewicz & Rokicki, 2007; Hryniewicz et al., 2007). Consequently, regarding reduction in hydrogenation, the results obtained by SIMS are in agreement with the sample surface roughness data concerning their mode of treatment (Hryniewicz et al., 2011).
Some of the studies on surface roughness performed by other technique (Atomic Force Microscopy, AFM) on Nitinol (Fig. 4) also confirm improvement of MEP treated samples against EP ones (Rokicki et al., 2008; Hryniewicz & Rokicki, 2008).

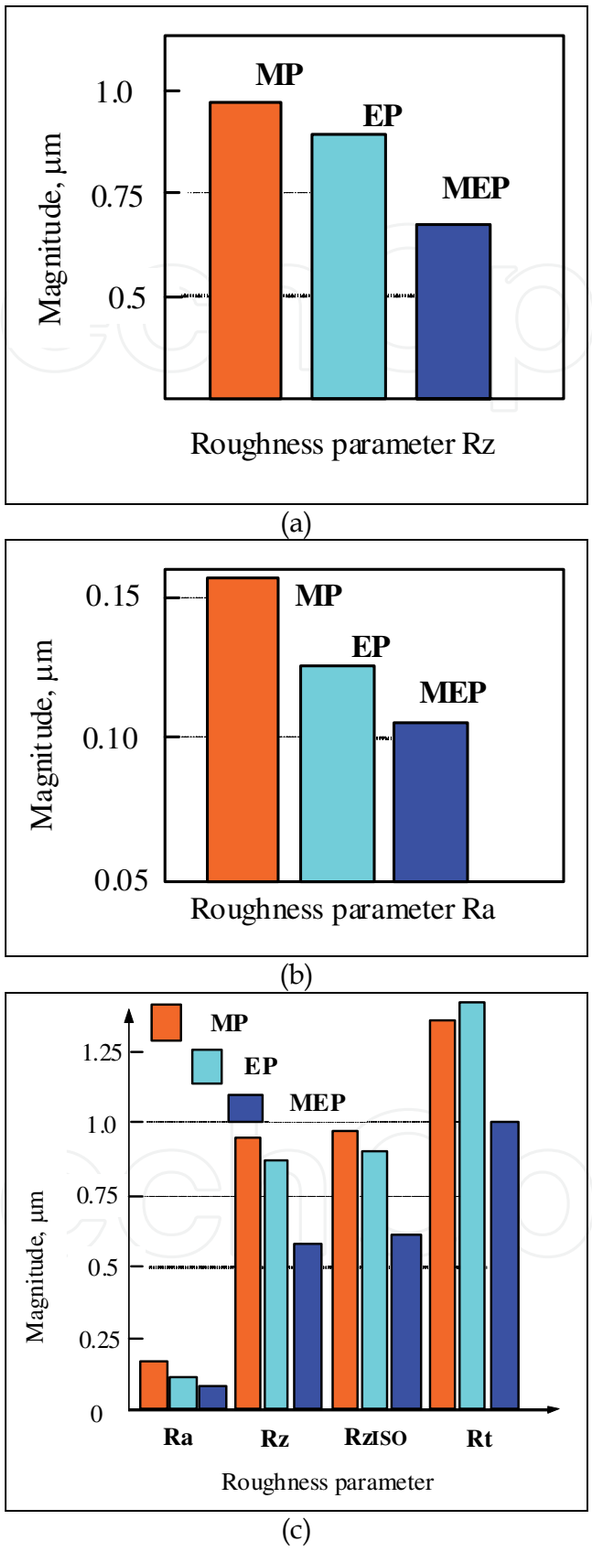


Fig. 2. Surface roughness parameters measured on a CP Ti Grade 2 wire: (a) R_z, (b) *Ra*, (c) comparison of *Ra*, R_z, R_zISO, *Rt*.

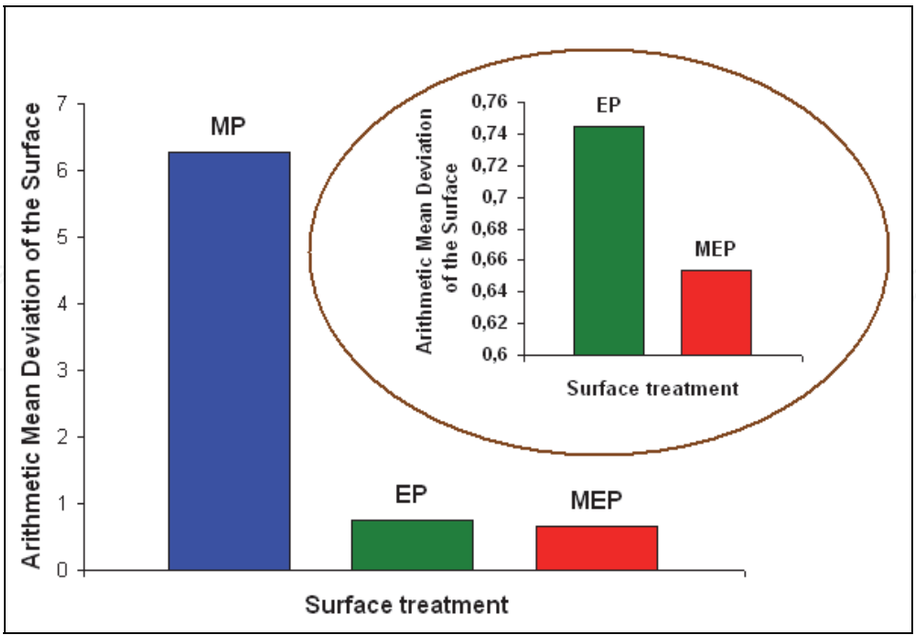


Fig. 3. *Sa* surface roughness parameter measured on a CP Ti Grade 2 strip after MP, EP, and MEP.

Treatment	*Sa*
MP	6.28
EP	0.745
MEP	0.654

Table 1. *Sa* data of interferometry studies performed on MP, EP, and MEP samples of CP Ti Grade 2.

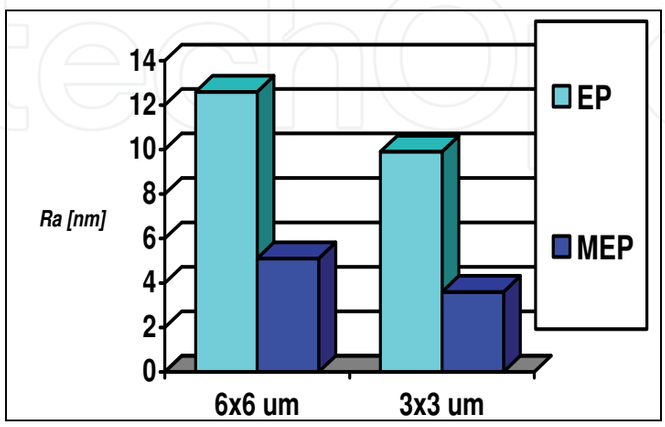


Fig. 4. Average surface roughness *Ra* parameter of Nitinol sample after EP, and MEP, measured by AFM (Rokicki et al., 2008).

6. Wettability and microscopic studies

The orthopaedic titanium implants can be divided in two groups. One group of implant consists of devices which after implantation will stay permanently in the body (spine implants). Second group covers implants which are temporarily implanted and after healing is over those devices are removed from the body (fracture fixation devices as bone plates, nail etc). The one of most desired property for permanent implants are their complete and strong osseointegration. For temporary devices the strong osseointegration is not desirable because it complicates removal procedure, which can lead to unnecessary blood loss, infection or even fracture. To accomplish this goal the metallic implants require different surface finish which was shown in recent work of Hayes et al., (2010).
It is well known that wettability of metallic implant surfaces plays great role in their bio integrity with surrounding tissues in titanium case most importantly with bones. In our study electropolished and magnetoelectropolished surfaces had shown very different wettability (Rokicki & Hryniewicz, 2008). The simple experiment with drop of water dragged upon the EP and MEP surface have shown very different behaviour. Dragged droplet of water on EP surface was leaving the trace behind; this indicates that surface is very hydrophilic. Contrary dragged droplet of water on magnetoelectropolished surface did not leave any traces and this indicates very hydrophobic surface property. Taking under consideration finding of Hayes et al. (2010) that electropolished titanium surface leads to lesser bone integration we hypothesize that more hydrophobic in our case magnetoelectropolished titanium surface should lead to better and more fuller osseointegration which will be very desirable for permanent orthopaedic implants.

7. Corrosion measurements

A metal corrodes if the electrode potential $E = E_{corr}$ is the corrosion potential and flowing current $i_a = -i_c = i_{corr}$ in the created cell is the corrosion current. The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler-Volmer equations:

$$i_a = i_{oa} \exp\left[2.303 \frac{E - E_{oa}}{b_a} \right] \tag{3}$$

$$i_c = i_{oc} \exp\left[2.303 \frac{E - E_{oc}}{b_c} \right] \tag{4}$$

where:
b_a, b_c – Tafel constants
i_{oa}, i_{oc} – exchange current densities for the anodic and cathodic processes, respectively
E_{oa}, E_{oc} – equilibrium potentials for the anodic and cathodic processes, respectively.
Summary current density:

$$i = i_a + i_c \tag{5}$$

then

$$i = i_{corr}\left(\exp 2.303\frac{\Delta E}{b_a} - \exp 2.303\frac{\Delta E}{b_c}\right) \tag{6}$$

where

$$\Delta E = E - E_{corr} \tag{7}$$

$$\left(\frac{\partial i}{\partial E}\right)_{E=E_{corr}} = R_t^{-1} = 2.303 i_{corr}\left(\frac{1}{b_a} + \frac{1}{b_c}\right) \tag{8}$$

and

$$i_{corr} = \frac{b_a b_c}{2.303(b_a + b_c)}\left(\frac{\partial i}{\partial E}\right)_{E=Ecorr} \tag{9}$$

The corrosion rate in the anodic sites on the metal surface is proportional to the current intensity. The current intensity flowing through the current cell results in change of potentials of both anodic (oxidation) and cathodic (reduction) reactions (Hryniewicz et al., 2009). The cathodic potential shifts into negative direction and anodic potential shifts into positive direction.

The GPES (General Purpose Electrochemical Software) provides a convenient interface for making Tafel plots, calculating Tafel slopes and corrosion rates. First we specify the anodic and cathodic Tafel region. Once the regions are selected the GPES software automatically calculates the Tafel slopes and the corrosion currents. A correct estimate of the Tafel slopes is possible only if the linear Tafel region covers at least one decade in current. Some additional data are the density of investigated material, equivalent mass, and the studied surface area. Having these the algorithm serves to calculate corrosion current density, polarization resistance, and the corrosion rate CR.

The corrosion studies of conventionally electropolished (EP) and magnetoelectropolished (MEP) titanium samples below oxygen evolution regime were carried out in a Ringer's solution (Table 2) at 25 °C (Figs. 5, and 6). Ringer's (*Solution Ringeri* by Fresenius Kabi) and Hank's solutions are the main artificially created human fluids generally recognized by the researchers to carry out the corrosion studies on biomaterials.

Solution components	g/dm^3	Ions	mEq/dm^3	mmol/dm^3
Sodium chloride	8.60	Na^+	147.16	147.16
Potassium chloride	0.30	K^+	4.02	4.02
Calcium chloride	0.48	Ca^{2+}	4.38	2.19
		Cl^-	156.56	156.56

Table 2. Ringer's solution composition used for the corrosion study.

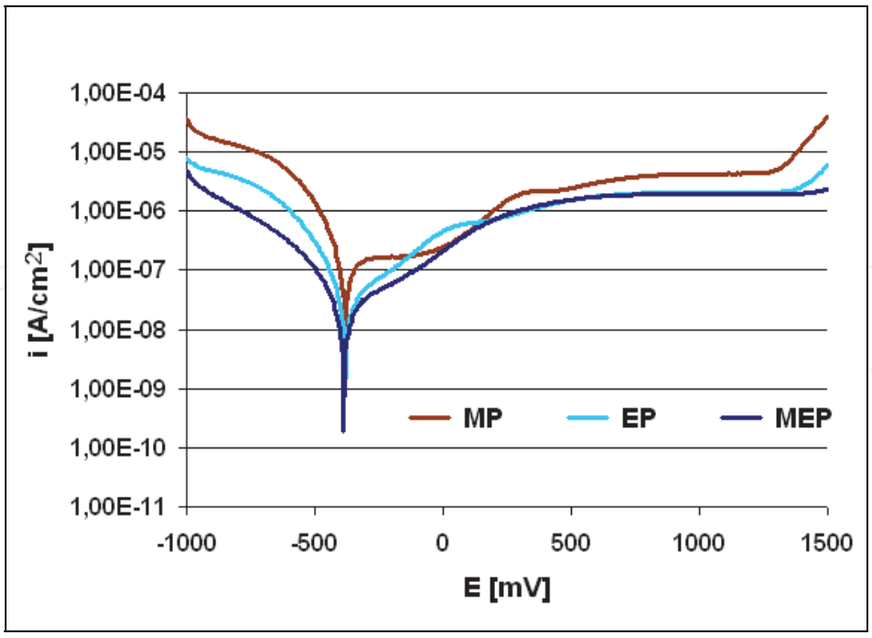


Fig. 5. Polarization cures of Ti samples in Ringer's solution after: MP – abrasive polishing, EP – standard electropolishing, MEP – magnetoelectropolishing.

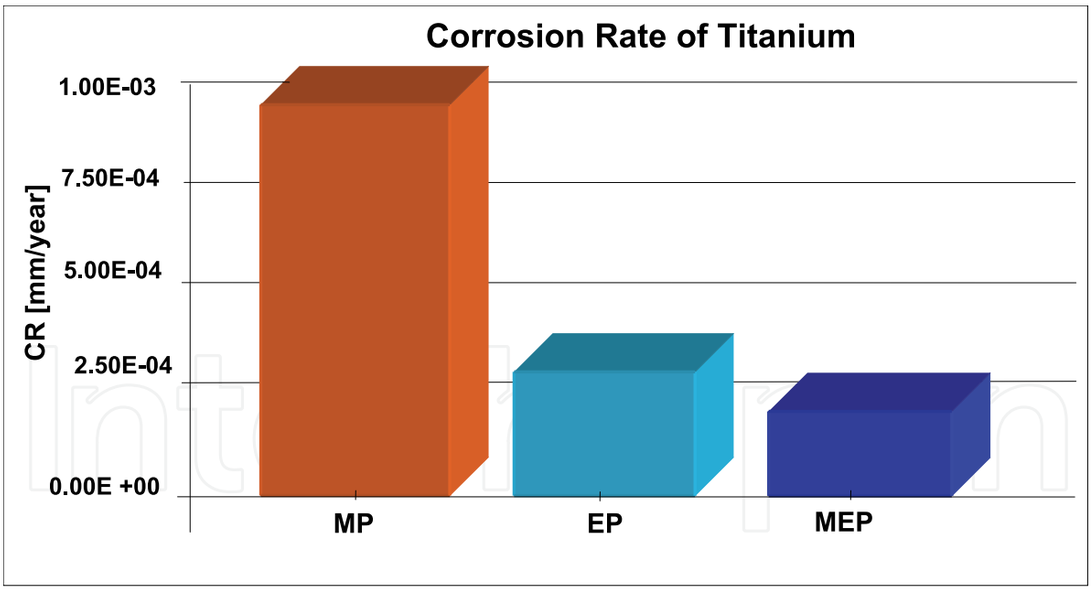


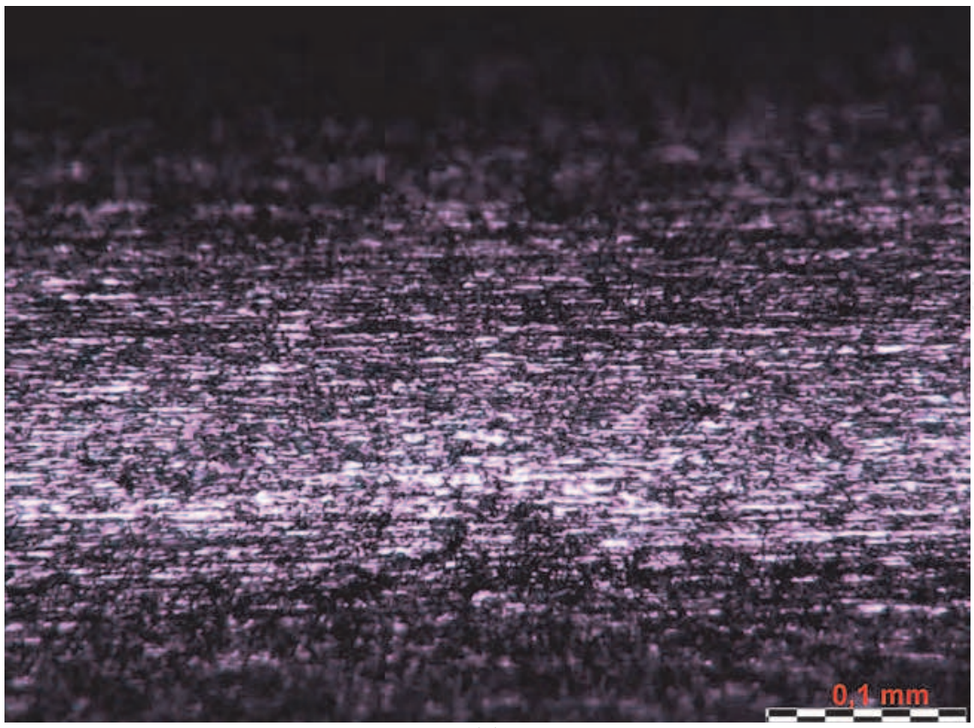
Fig. 6. Comparison of corrosion rates of Ti samples in Ringer's solution after: MP – abrasive polishing, EP – standard electropolishing, MEP – magnetoelectropolishing.

In the corrosion studies, polarization curves obtained on Ti samples in Ringer's solution (Fig. 5) indicated a significant differentiation in their courses dependent on the treatment mode considered. Calculated corrosion rates CR (Fig. 6) reveal even more clearly the decrease in CR after electropolishing (EP), and further reduction in CR is observed after MEP process.

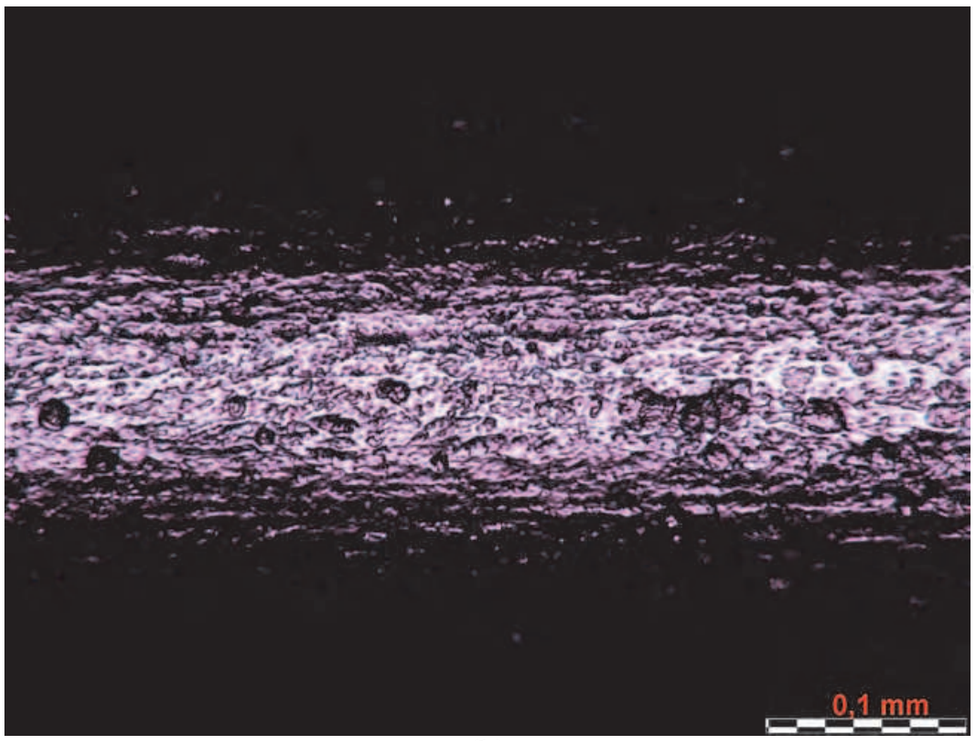
The microscopic observations of the Ti samples after EP, MEP and MP were performed to compare the results of the study ((2) Hryniewicz et al., 2009). The pictures which were taken by Neophot and SEM very well characterize visually the Ti surface after each of the treatment performed. The example images of the wire samples are presented in Fig. 7. Changes in surface topography after MP, EP, and MEP may be viewed, showing the smoothest surface after MEP (Fig. 7c). Fig. 7a presents the typical surface pattern after abrasive pretreatment, whereas Ti image after EP (Fig. 7b) shows multiple irregularities and cavities. The reason of increased fatigue resistance of titanium biomaterial after MEP was due to different plastic behaviour of the same Ti wire after two electropolishing treatments, EP and MEP (Hryniewicz et al., 2009).

8. XPS surface film composition studies

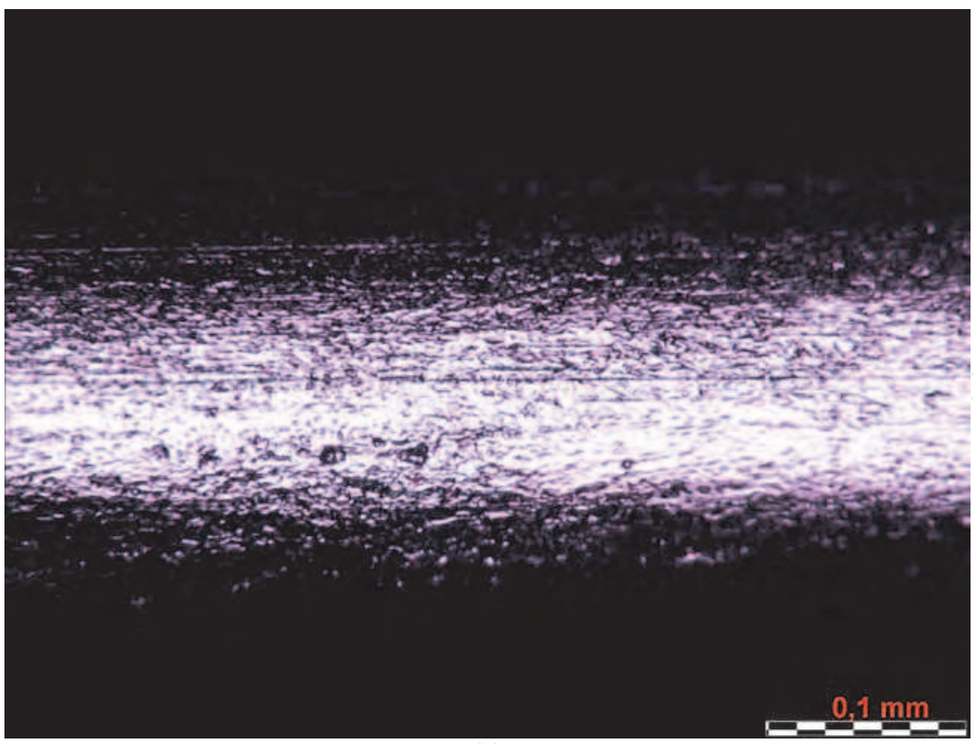
Surface film composition on wire samples of CP Ti (commercial purity titanium) Grade 2 after a standard electropolishing (EP), magnetoelectropolishing (MEP), compared with mechanically polished (MP) samples was studied and the results presented in consecutive Figs. 8, 9, 10, and in Table 3. In Fig. 8, the high resolution XPS (X-ray Photoelectron Spectroscopy) spectra of CP-Ti samples after MP, EP, and MEP, are compared. Characteristic peaks of titanium and oxygen may be observed, with a carbon peak coming from environment, occurring always in this kind of studies.
In Figs. 9a-f, the results of surface film composition measured on titanium samples are presented. Figs. 9a,b show the results after MP, Figs. 9c,d – after EP, and Figs. 9e,f – after MEP. In Figs. 9 (a, c, e) spectra are referred to titanium (Ti^0, Ti^{2+}, Ti^{3+}, Ti^{4+}), and in Figs. 9 (b, d, f) spectra are referred to oxygen group (O^{2-}, OH^-, H_2O).



(a)



(b)



(c)

Fig. 7. Micrographs of Ti wire sample surfaces after: (a) MP – abrasive polishing, (b) EP – standard electropolishing, (c) MEP – magnetoelectropolishing.

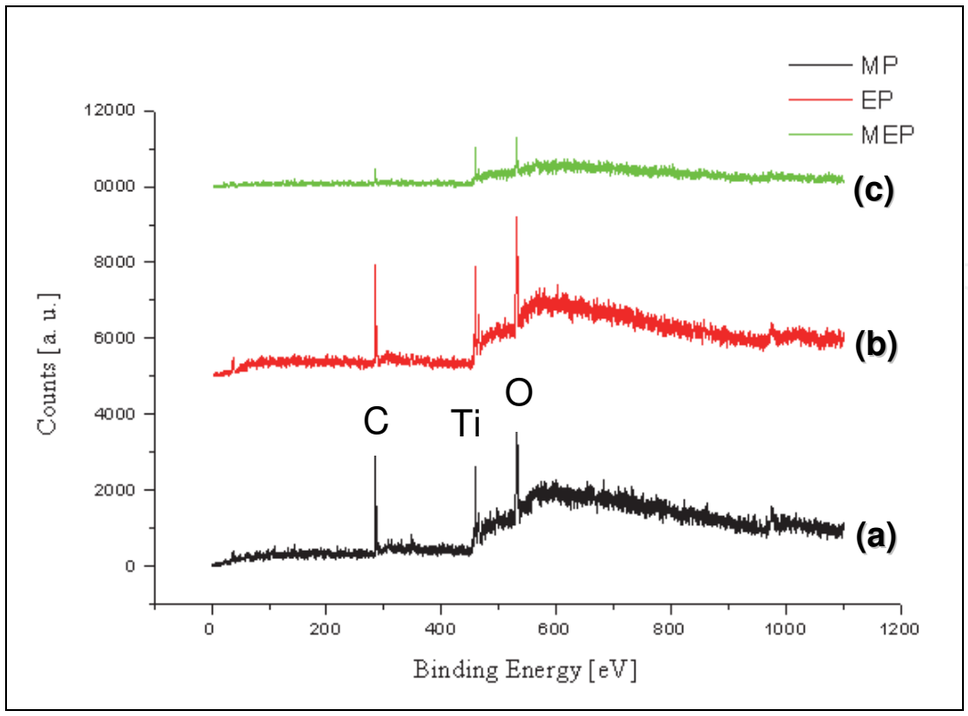
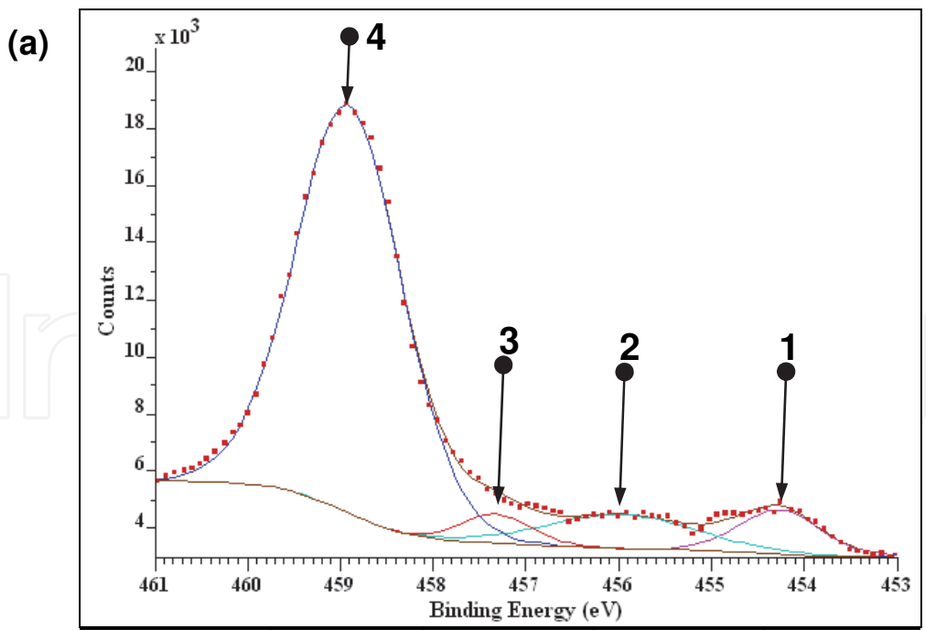
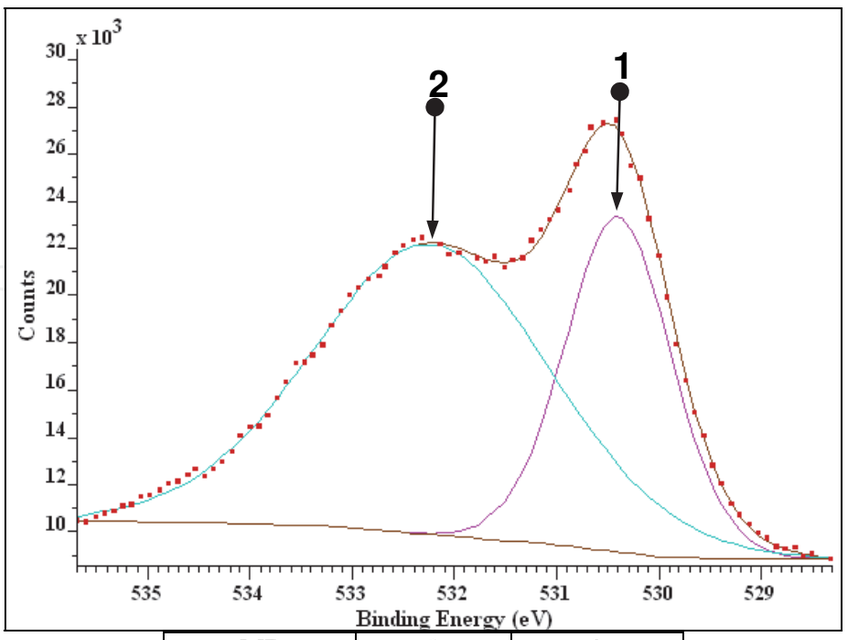


Fig. 8. High resolution XPS spectra of Ti samples (wires) comparison obtained on surface: (a) as-received MP, (b) after EP, (c) after MEP.



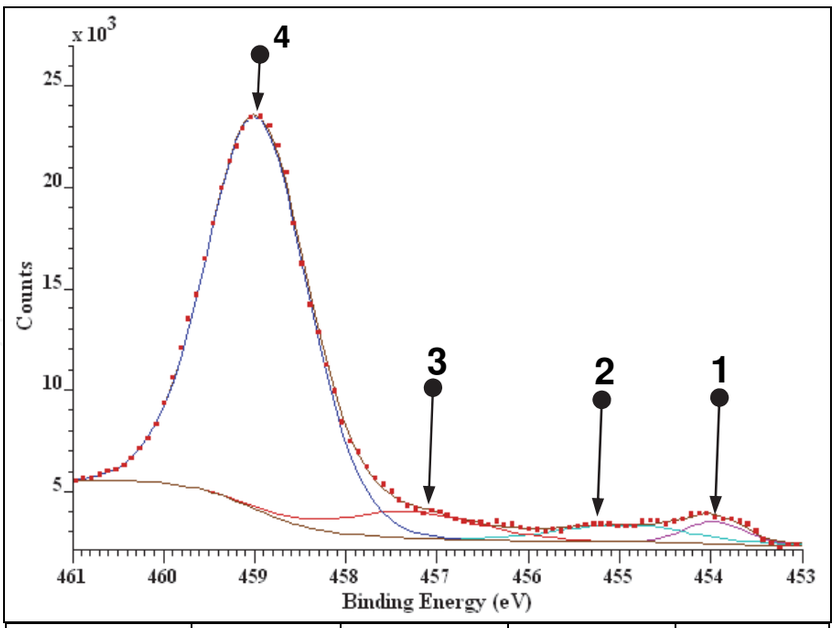
MP	1	2	3	4
BE [eV]	454.267	455.97	457.331	458.906
FWHM	1.034	1.893	0.877	1.356
MPC	Ti^{0}	Ti^{2+}	Ti^{3+}	Ti^{4+}
	7%	9%	4%	80%

(b)



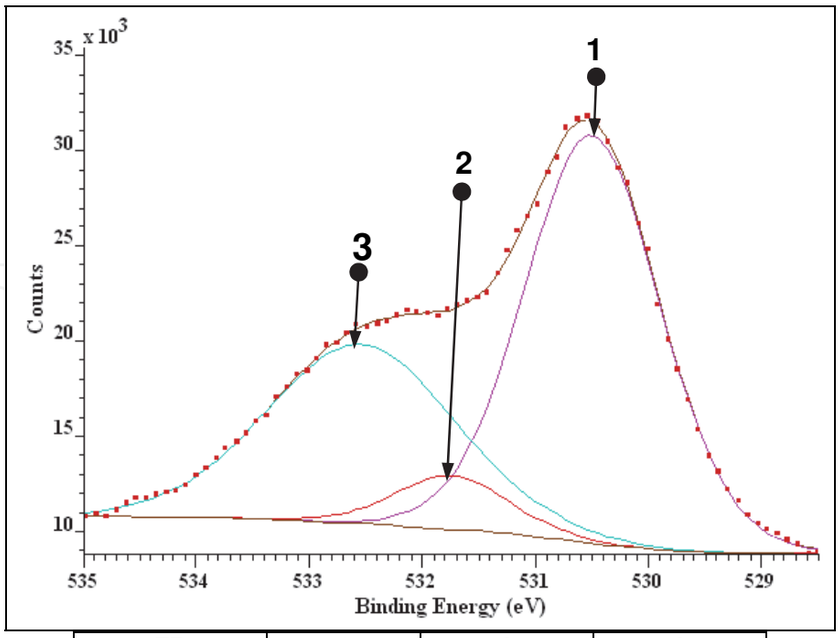
MP	1	2
BE [eV]	530.4	532.226
FWHM	1.215	2.732
MPC	O^{2-}	H_2O
	34%	66%

(c)



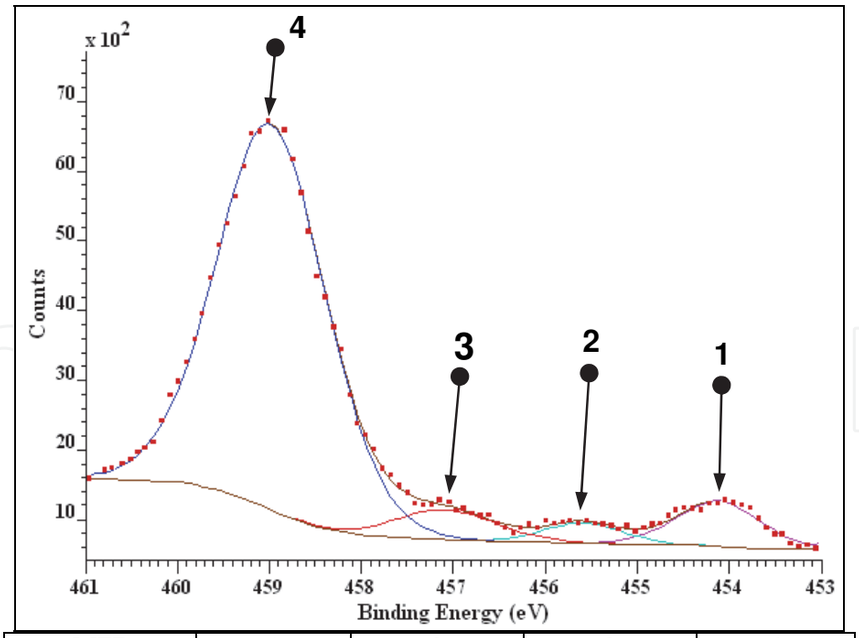
EP	1	2	3	4
BE [eV]	453.953	454.923	457.316	458.971
FWHM	0.776	1.687	1.747	1.309
MPC	Ti^0	Ti^{2+}	Ti^{3+}	Ti^{4+}
	3%	5%	8%	84%

(d)

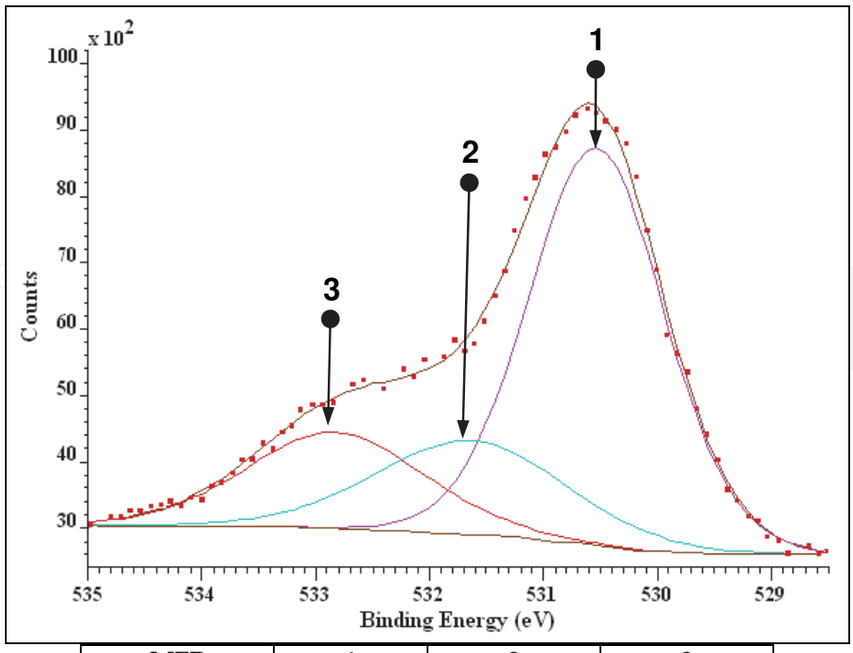


EP	1	2	3
BE [eV]	530.498	531.738	532.544
FWHM	1.408	1.172	1.962
MPC	O^{2-}	OH^{-}	H_2O
	58%	8%	34%

(e)



MEP	1	2	3	4
BE [eV]	454.126	455.589	457.092	458.978
FWHM	1.057	0.964	1.256	1.391
MPC	Ti^{0}	Ti^{2+}	Ti^{3+}	Ti^{4+}
	7%	3%	6%	84%



MEP	1	2	3
BE [eV]	530.535	531.637	532.835
FWHM	1.404	1.965	1.829
MPC	O^{2-}	OH^-	H_2O
	61%	20%	19%

Fig. 9. Surface film composition measured by XPS of the treated CP Ti Grade 2 for 3 samples (wires) after: (a, b) mechanical polishing MP, (c, d) electrochemical polishing EP, (e, f) magnetoelectropolishing MEP; (a, c, e) spectra referred to titanium (Ti^0, Ti^{2+}, Ti^{3+}, Ti^{4+}), (b, d, f) spectra referred to oxygen group (O^{2-}, OH^-, H_2O). Under description:

- **BE** – binding energy
- **FWHM** – an expression of the extent of a function, given by the difference between the two extreme values of the independent variable at which the dependent variable is equal to half of its maximum value
- **MPC** – most probably compound

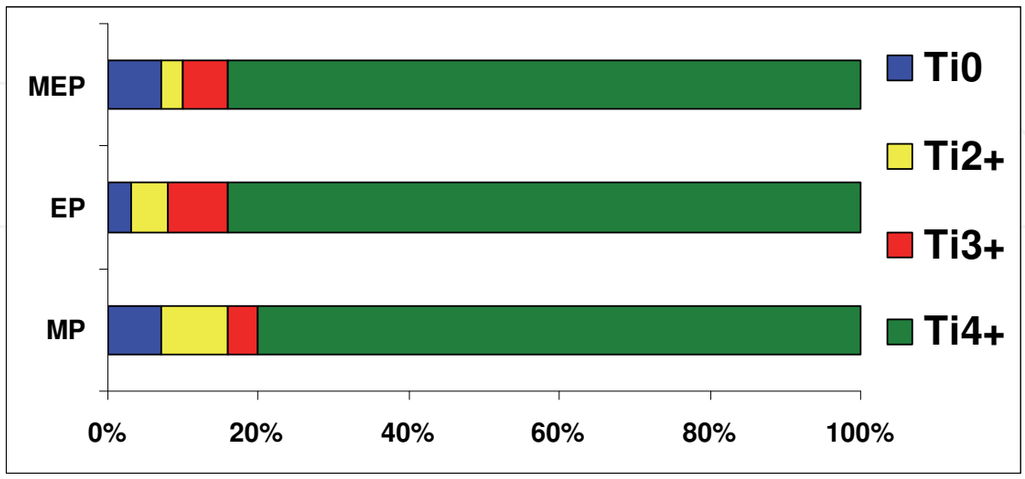
Each of the presented plots in Fig. 9 has been connected with the underlying Table 3 revealing all important data, indicating the most probable compound (MPC) with the relevant percentage in Ti surface film investigated.

Treatment	Ti^0	Ti^{2+}	Ti^{3+}	Ti^{4+}
MP	7%	9%	4%	80%
EP	5%	5%	8%	84%
MEP	7%	3%	6%	84%

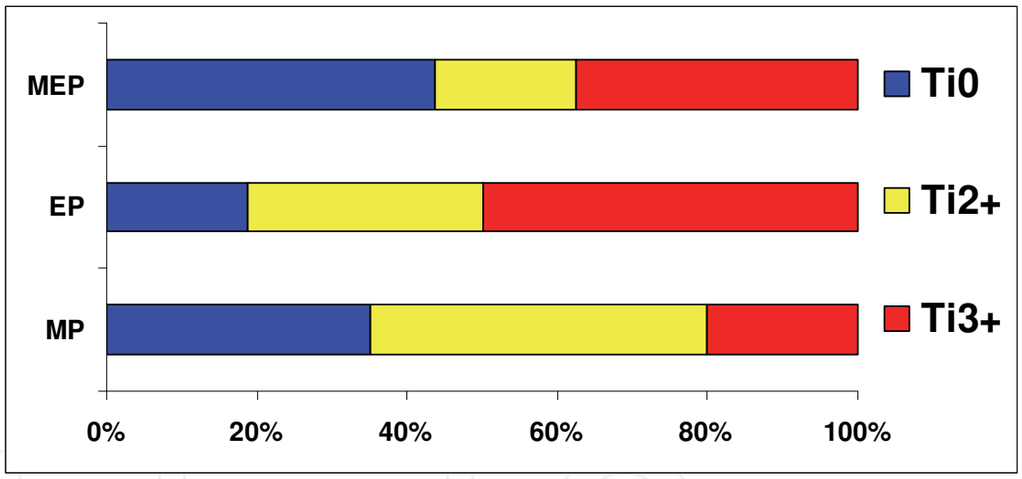
Table 3. XPS data of the treated CP Ti Grade 2 for 3 samples (strips).

The most interesting spectra referred to titanium (Ti^0, Ti^{2+}, Ti^{3+}, Ti^{4+}), concerning Fig. 9 (a, c, e), have been gathered and reported in Table 3. Visual presentation of the results is given in

Fig. 10. In Fig. 10a the comparison with full presentation is given, and in Fig. 10b there are shares excluding Ti^{4+} reported. Depending on the surface treatment used, characteristic differentiation in composition of surface film is apparent.



(a)



(b)

Fig. 10. Surface film composition by XPS of the treated CP Ti Grade 2 for 3 samples (strips): (a) shares with full representation, (b) shares excluding Ti^{4+}.

9. Fatigue resistance

Our extensive studies over metallic biomaterials show that the kind of finish affects also some mechanical properties. The experiments carried out on samples of CP-titanium and Ti-alloys (Nitinol) indicate that electropolishing (EP) greatly affects the resistance to bending in advantage of this process against abrasive polishing (MP), and the results obtained on samples after MEP are better than those recorded after a standard EP process (Fig. 11). Our research study results performed on fatigue resistance according to the Polish Standard (1975) have been also confirmed by another team of authors on finished by us commercial endodontic files (Praisarnti et al., 2010).

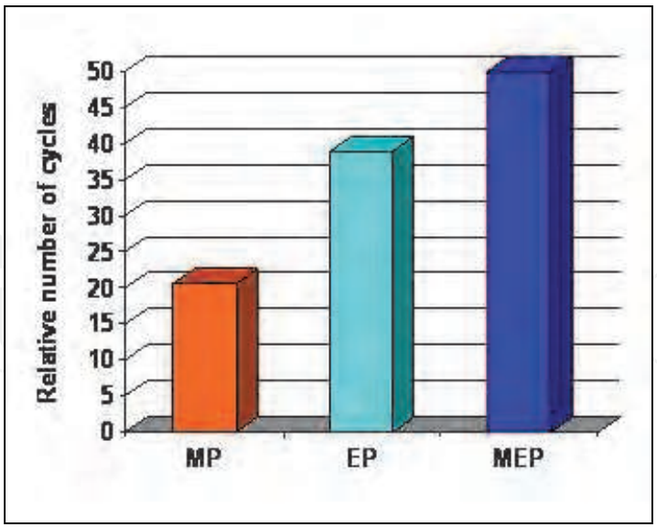


Fig. 11. Relative resistance to bending of Ti samples after: MP – abrasive polishing, EP – standard electropolishing, MEP – magnetoelectropolishing.

10. Conclusion

Selection of titanium and titanium alloys with relatively high strength for critical high-temperature, corrosive environment application in the twentieth century was limited to those commercial alloys developed and designed specifically for aerospace use. Most commercial titanium and Ti alloys were not fully resistant to localized attack and/or stress corrosion in chloride environments.

Titanium (and its alloys), though long known, has found favour in recent years as biomaterial. As a biomaterial, titanium is widely used for surgical and medical implants, both skeletal and dental. The state of the surface finish is critical, and numerous studies have shown the benefits of electropolishing, with advantageous using of magnetic fields.

The application of externally applied magnetic fields to the electropolishing process provides the super-critical refinement of surface properties to the new high level required for medical implant devices. Improved corrosion resistance of magnetoelectropolished titanium surface is caused by more homogenized amorphous mixture of titanium oxides and hydroxides compared with very crystalline titanium oxide mainly in rutile form on conventionally electropolished surface.

The following final conclusions may be drawn after investigation of titanium biomaterial:

a. a new improved technology effective for titanium biomaterial has been offered
b. the surface roughness after MEP is much less than after a standard EP; all detected roughness parameters after MEP were better than those after EP
c. very good corrosion characteristics have been obtained with the best performance corrosion potential after MEP; the highest corrosion resistance has been obtained on samples after MEP ($CR=1.84\times10^{-4}$ mm/year), the worst one after MP ($CR=9.63\times10^{-4}$ mm/year), and $CR=2.67\times10^{-4}$ mm/year after EP (Figs. 5 and 6)
d. Ti biomaterial samples after MEP appeared to be the most resistant to fracture, of about 27% better than the same Ti samples after EP, and much better than after abrasive polishing MP (Fig. 11).

It was found that titanium biomaterial properties may be well improved after using a new technology utilizing the magnetic field during electrolytic polishing. This study shows that both titanium and titanium alloys for medical applications may be considerably improved.

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These contribution books collect reviews and original articles from eminent experts working in the interdisciplinary arena of biomaterial development and use. From their direct and recent experience, the readers can achieve a wide vision on the new and ongoing potentials of different synthetic and engineered biomaterials. Contributions were not selected based on a direct market or clinical interest, than on results coming from very fundamental studies which have been mainly gathered for this book. This fact will also allow to gain a more general view of what and how the various biomaterials can do and work for, along with the methodologies necessary to design, develop and characterize them, without the restrictions necessarily imposed by industrial or profit concerns. The book collects 22 chapters related to recent researches on new materials, particularly dealing with their potential and different applications in biomedicine and clinics: from tissue engineering to polymeric scaffolds, from bone mimetic products to prostheses, up to strategies to manage their interaction with living cells.

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