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Measurements of nanohardness and elasticity modulus of titanium after magnetoelectropolishing

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Abstract

Nanohardness is one of the main mechanical properties of the studied metal surface after electropolishing operations. The nanoindentation measurements were performed on CP-titanium biomaterial after its treatment under a standard electropolishing (EP) and magnetoelectropolishing (MEP) conditions, with abrasive polishing (MP) performed on the samples for reference. In the studies, both the Young's modulus of elasticity and nanohardness were investigated. It was found that the mechanical properties of titanium biomaterial indicated an evident dependence on the type and conditions of surface treatment. After magnetoelectropolishing (MEP) operation a considerable change in mechanical properties of the same Ti biomaterial was observed. One may state that the mechanical properties obtained on the titanium samples both after abrasive polishing (MP) and after a standard electropolishing (EP) are very different from those gained on the magnetoelectropolished titanium sample.

Słowa kluczowe: Nanoindentation; Titanium biomaterial; Nanohardness; Young's modulus; Magnetoelectropolishing MEP.

Pomiary nanotwardości i modułu sprężystości tytanu po magnetoelektropolerowaniu

Streszczenie

Nanotwardość jest jedną z ważniejszych cech mechanicznych powierzchni metali po obróbce elektropolerowaniem. W tradycyjnych badaniach twardości materiału, diamentowa końcówka wgłębnika służy badaniu twardości i modułu sprężystości. Pod obciążeniem wgłębnika następują odkształcenia sprężyste i plastyczne. Dobór wielkości obciążenia uzależniony jest od celu badania – samego materiału, czy też warstewek pasywnych powstałych na powierzchni metalu po określonej obróbce wykończającej. W artykule przedstawiono wyniki pomiarów metodą nanoindentacji próbek tytanu o czystości komercyjnej po polerowaniu elektrolitycznym w warunkach standardowych (EP), i magnetoelektropolerowaniu (MEP), oraz po polerowaniu ściernym (MP) próbek, które posłużyły jako odniesienie. Badano moduł sprężystości Younga oraz nanotwardość materiału. Wyniki badań pokazują, że własności mechaniczne tytanu zależą od rodzaju i warunków obróbki wykończającej. Po magnetoelektropolerowaniu (MEP) wyniki nanoindentacji różnią się zasadniczo od analogicznych wyników uzyskanych po standardowym elektropolerowaniu (EP) i po polerowaniu ściernym (MP). Taka zmiana zasadniczo wpływa na poprawę odporności na przeginanie, zginanie i skręcanie biomateriału.

Keywords: nanoindentacja, tytan, magnetoelektropolerowanie MEP, nanotwardość, moduł Young'a.

1. Introduction

Among the various metallic biomaterials, such as stainless steels and Co-Cr alloys, titanium and its alloys exhibit the best biocompatibility. This specific feature together with the Young's modulus of bulk titanium made this material to be of great importance and value [1-3]. Titanium offers outstanding resistance to a wide variety of environments. The metal's corrosion resistance is due to a stable, protective, strongly adherent oxide film. Low density and high strength of titanium commend it for use in a variety of accessories applied in every-day life, electronics, and marine fittings such as cleats and winches. Its resistance to saltwater corrosion far exceeds that of anodized aluminum. Titanium and its alloys provide excellent resistance to general localized attack under most oxidizing, neutral and inhibited reducing conditions. Such specific properties and features make titanium as one of the most valued biomaterial widely used for surgical and medical implants, both skeletal and dental [4].

It is well known that surface finish may highly affect mechanical and physical properties of metals and alloys. Our earlier studies [4, 5] indicated a considerable dependence of mechanical properties of titanium on the surface treatment method used. Electrochemical polishing is one of essential surface technology used for metals and alloys. Recently the magnetic field was introduced to modify the process of electropolishing [4-6]. In fact it resulted in a significant improvement of some mechanical properties, including also changes in indentation results [4, 6]. It appears the material hardness is an important magnitude of material's characteristics. The significance of quantitative determination of material hardness was stressed in the authors' other work [7].

In a traditional indentation test the bulk material properties undergo the evaluation. Under the studies, a hard tip, usually made of diamond with known mechanical properties, is pressed into a sample whose properties are unknown. The load, placed on the indenter tip, is increased as the tip penetrates further into the specimen and soon reaches a user-defined value. The load may be held constant for a period or removed. The area of the residual indentation in the sample is measured and the hardness, H, is defined as the maximum load, P_{max}, divided by the residual indentation area, A_r [8-10].

The two mechanical properties measured most frequently using indentation techniques are the hardness H, and the elastic modulus E. As the indenter is pressed into the sample, both elastic and plastic deformations occur, resulting in the formation of a hardness impression according to the shape of the indenter. During indenter withdrawal, only the elastic portion of the displacement is recovered. A hard tip whose mechanical properties are known, usually made of a very hard material like diamond, is pressed into a sample whose properties are unknown [10].

Nanoindentation was recently investigated in other authors' works [4, 6], including presentation of the test instrument [6]. During the experiment, a variety of indentation hardness tests is applied to small volumes. Nanoindentation hardness is defined as the indentation load divided by the projected contact area of the indentation. Both elastic and plastic deformations occur under the penetration cycle and only the elastic portion of the displacement is recovered during unloading [10]. Nanoindentation hardness H is defined as:

$$H = \frac{P_{\max}}{A} \tag{1}$$

where $P_{\max}$ is the load measured at a maximum depth of penetration (h) in an indentation cycle; A is the projected contact area.

Conventional nanoindentation methods for calculation of modulus of elasticity (based on the unloading curve) are limited to linear, isotropic materials. It is known that the reduced Young's modulus E_r of the contact between the indenter and the sample has been determined [6] by:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \tag{2}$$

where E and ν are the elastic modulus and Poisson ratio for the sample, respectively, and E_i and ν_i are the same quantities for the indenter. For the diamond indenter $E_i = 1141$ GPa and $\nu_i = 0.07$ [6].

The aim of the work is presenting changes in mechanical properties of titanium as one of the most important and advanced biomaterial, used also for many other applications. The studies have been concerned upon the nanoindentation results obtained on titanium samples prepared by abrasive mechanical polishing (MP) and some meaningful finishing electrochemical operations, regarding standard electropolishing EP, and magnetoelectropolishing MEP.

2. Experimental method

CP Titanium Grade 2 biomaterial was manufactured in the form of big slabs from which Ti samples were acquired for the studies. Chemical composition of the used commercial purity CP Ti Grade 2 (at%) is given in Table 1. A set of titanium samples of dimensions 180×10×2 mm was prepared by a water jet cutting from a big slab. Such obtained Ti samples were treated using three methods: (a) abrasive polishing with SiC grit up to #1000, used as a reference, (b) a standard electropolishing (EP) process, and (c) electropolishing using a magnetic field, known as magnetoelectropolishing (MEP) [3, 4].

Tab. 1. Chemical constituents of CP Ti Grade 2 (at%, balance titanium). Manufacturer: INCONAS, Praha, Czech Republic

Tab. 1. Skład chemiczny badanego tytanu CP Ti Grade 2 (at%, reszta tytan). Wytwórca: INCONAS, Praga, Republika Czeska

O	N	C	H	Fe
0.25	0.03	0.08	0.015	0.3
Al	V	Ni	Mo	Other
-	-	-	-	0.4

For electropolishing operations, a proprietary electrolyte was used; it was a mixture of nonhalogen acid and alcohol. A nonhalogen electrolyte was applied to exclude the possibility of incorporating Cl^-, or F^- ions into the oxide. A constant external magnetic field below 0.5 T was applied to the EP system by neodymium ring magnets. The magnetic field was positioned parallel to the surfaces of the electropolished sample. A standard parallel EP experiment was conducted under the same conditions excluding the magnetic field in order to compare and evaluate differences apparent between Ti surfaces after EP and MEP [20]. Then, for the nanoindentation studies, such prepared plates were again disposed to cut off specimens of dimensions 10×8 mm to fix them in a holder.

Such prepared specimens were subjected to the nanoindentation measurements. The experiments were performed on the 950 TriboIndenter™ Nanomechanical test instrument [10]. The TI 950 TriboIndenter is the next-generation nanomechanical test instrument providing very good sensitivity and unprecedented performance. From the numerous nanomechanical testing techniques currently offered, as well as new testing methods currently being developed, quasistatic nanoindentation was applied to measure some mechanical properties. The nanoindentation was used to measure the Young's modulus, and nanohardness. Investigation of time-dependent properties of titanium biomaterial samples, using a dynamic testing technique, was performed by a nanoDMA™ [10].

Specimens for nanoindentation studies were identified by SEM with the images presented in Fig. 1. The Ti surface after separating by means of a water jet technique is presented in Fig.

1a, the one polished mechanically – in Fig. 1b, and electrolytically – after EP in Fig. 1c, and after MEP in Fig. 1d.

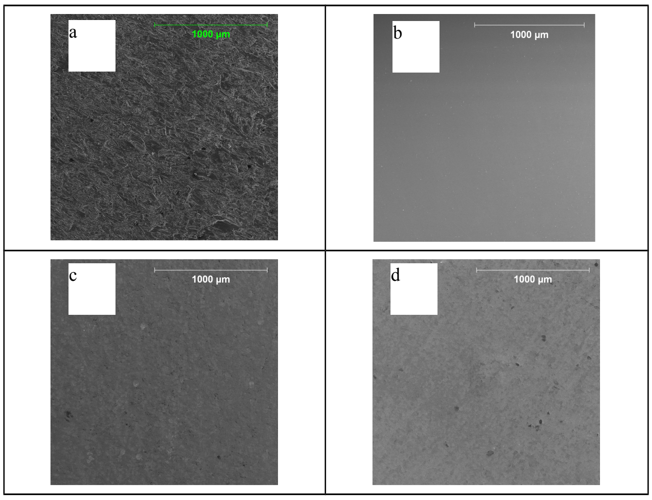

Fig. 1. Images of Ti samples after: (a) WJ water jet cut off, (b) abrasive polishing MP (using SiC #1000), (c) electropolishing EP, (d) magnetoelectropolishing MEP

Rys. 1. Mikrografie powierzchni próbek Ti po: (a) odcięciu strumieniem wody, (b) polerowaniu ściernym MP (ziarno SiC #1000), (c) elektropolerowaniu EP, (d) magnetoelektropolerowaniu MEP

3. Results of the study

Mechanical characteristics of titanium biomaterial, presenting force versus displacement, were studied after three finishing operations: (a) MP, (b) EP, and (c) MEP. Therefore three bunches of load-displacement curves after nanoindentation measurements were obtained, and they are presented in Fig. 2.

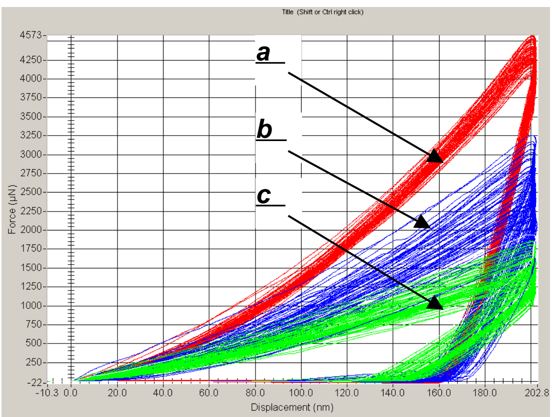

Fig. 2. Mechanical behaviour of Ti biomaterial samples, force vs. displacement, examined after: (a) mechanical/abrasive polishing (MP), (b) electropolishing (EP), (c) magnetoelectropolishing (MEP)

Rys. 2. Mechaniczne zachowanie się tytanu, siła w funkcji przemieszczenia, po: (a) polerowaniu mechanicznym MP, (b) elektropolerowaniu EP, (c) magnetoelektropolerowaniu MEP

One may easily observe considerable changes in the curves courses between MP, EP and MEP titanium samples. The steepest course was obtained on Ti specimen surface after abrasive polishing MP (Fig. 2a), and the lowest – after magnetoelectropolishing MEP (Fig. 2c), with the surface after a standard electropolishing EP running in between (Fig. 2b). Such a behaviour clearly proves of differentiation between these three states of titanium surface.

Presentation of determination of reduced Young's modulus and nanohardness of titanium samples after MP, EP and MEP treatments is given in Fig. 3. The recorded mechanical data for three titanium samples vary concerning the curves and slopes/tangents. One may notice the differentiation in values of the reduced Young's modulus and nanohardness obtained on the same biomaterial, dependent on the method of the finishing treatment, referred to: (a) MP, (b) EP, and (c) MEP.

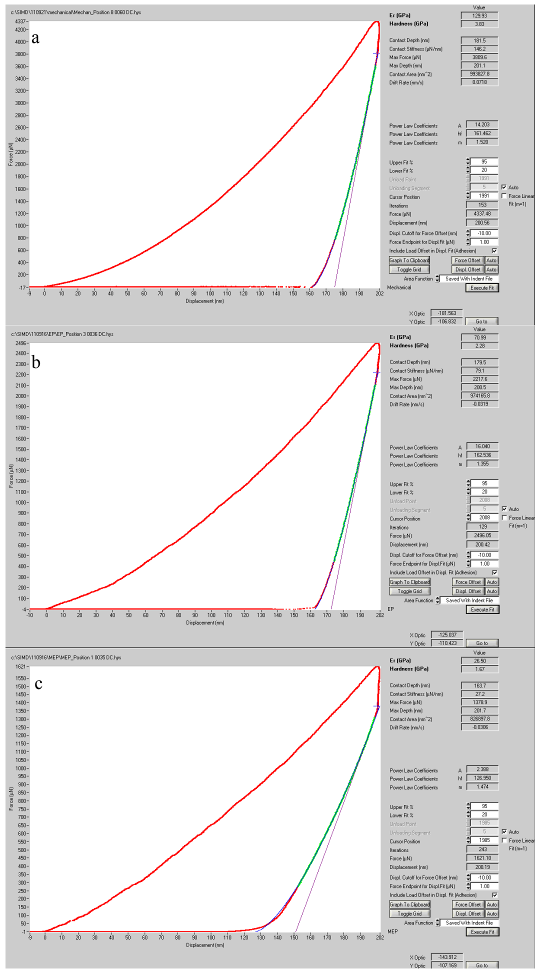

Fig. 3. Results of nanohardness measurements of Ti biomaterial samples, force vs. displacement, examined after: (a) mechanical/abrasive polishing (MP), (b) electropolishing (EP), (c) magnetoelectropolishing (MEP)

Rys. 3. Wyniki pomiarów nanotwardości próbek Ti, siły w funkcji przemieszczenia, zbadane po: (a) polerowaniu ściernym MP, (b) elektropolerowaniu EP, oraz (c) magnetoelektropolerowaniu MEP

The study results of nanohardness and the reduced Young's modulus as the function of the contact depth measured on titanium sample surface after MP (a), EP (b), and MEP (c) treatments are revealed in Fig. 4.

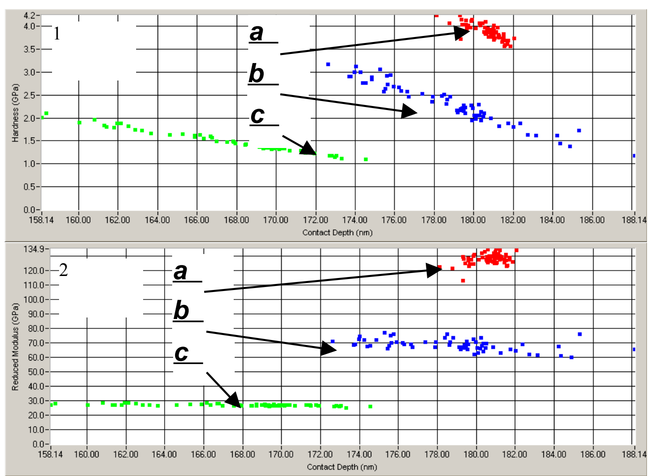

Fig. 4. Nanoindentation results of: (1) nanohardness vs. contact depth, (2) reduced Young's modulus vs. contact depth measurements of Ti biomaterial samples, examined after: (a) mechanical/abrasive polishing (MP), (b) electropolishing (EP), and (c) magnetoelectropolishing (MEP) [4]

Rys. 4. Wyniki badań nanoindentacji tytanu: (1) nanotwardości w funkcji głębokości, (2) zredukowanego modułu Young'a w funkcji głębokości po: (a) polerowaniu ściernym MP, (b) elektropolerowaniu EP, (c) magnetoelektropolerowaniu MEP [4]

It can be easily noticed that the results of nanoindentation of the same titanium biomaterial after different surface treatments are spread under three varying conglome-rations [4]. The results after magnetoelectropolishing MEP (a) significantly depart form the ones obtained on samples after MP, and EP treatments concerning both nanohardness (Fig. 4(1)), and reduced modulus E_r (Fig. 4(2)). They are spread linearly on the bottom part of the plot distanced from both the results obtained after a standard electropolishing EP (b), and much further after abrasive polishing MP (a), respectively. Such a behaviour means, as it results from Eq. (2), that the reduced elastic modulus E_r is the lowest in case of the titanium sample after MEP treatment in comparison with the ones of the same titanium biomaterial noticed after EP (higher), and MP (the highest).

Nanoindentation measurement results of titanium biomaterial samples obtained after (a) abrasive polishing MP, (b) standard electropolishing EP, and (c) magnetoelectropolishing MEP are presented in Table 2. The Table 2 covers digital estimates/mean values and standard uncertainties.

Tab. 2. Nanoindentation measurement digital results of Ti biomaterial samples, obtained after: (a) mechanical/abrasive polishing (MP), (b) electropolishing (EP), (c) magnetoelectropolishing (MEP)

Tab. 2. Liczbowe wyniki pomiarów nanoindentacji uzykane na próbkach biomateriału Ti po: (a) polerowaniu mechanicznym/ściernym (MP), (b) elektropolerowaniu (EP), (c) magnetoelektropolerowaniu (MEP)

Treatment method	Quantity	h_c (nm)	E_r (GPa)	H (GPa)
a	Estimate	180.67	127.97	3.88
MP	Standard uncertainty	0.8076	3.58	0.1591
b	Estimate	178.72	68.56	2.31
EP	Standard uncertainty	3.25	3.87	0.4565
c	Estimate	167.84	26.94	1.47
MEP	Standard uncertainty	3.90	0.6705	0.2370

Comparison results of nanohardness and reduced Young's modulus of titanium samples at the contact depth of 174 nm are shown in Fig. 5. The lowest value of nanohardness (about 1.1 GPa) at the determined contact depth was obtained after MEP (Fig. 5c), much higher (about 3 GPa) after EP (Fig. 5b), and the highest (about 4.3 GPa) after MP (Fig. 5a).

Fig. 5. Relative results of hardness and reduced Young's modulus of Ti biomaterial samples at contact depth of 174 nm measured after: (a) mechanical/abrasive polishing (MP), (b) electropolishing (EP), (c) magnetoelectropolishing (MEP). (For standard uncertainties – see Table 2)

Rys. 5. Wyniki pomiarów nanotwardości i zredukowanego modułu Young'a E_r dla tytanu przy zagłębieniu 174 nm po: (a) polerowaniu ściernym MP, (b) elektropolerowaniu EP, oraz (c) magnetoelektropolerowaniu MEP. Standardowe niepewności podano w Tablicy 2

Considering the reduced Young's modulus, here also the highest value is obtained after MP (about 135 GPa), much lower after EP (about 70 GPa), and the lowest in the sample surface after MEP (about 27 GPa). Such differentiated results, obtained during nanoindentation measurements of titanium biomaterial, indicate that they must affect many other characteristics of that metal, regarding both thickness and composition of the surface oxide-hydroxide layer formed after each of the treatments: MP, EP, and MEP. On the other hand, that differentiation clearly influences the corrosion resistance [3] as well as other mechanical behaviours, such as resistance to bending, torsion and tension/stretching [4-6, 12].

4. Conclusion

Two essential mechanical properties, the Young's modulus of elasticity and nanohardness of CP-Ti, were investigated using nanoindentation technique. They both have revealed a clear dependence on the surface treatment method used, in this the electropolishing parameters and its conditions. After magneto-electropolishing MEP operation a considerable decrease in the Young's modulus of the same Ti biomaterial is observed in comparison with the ones obtained after abrasive polishing MP and a standard electropolishing (EP).

The study results indirectly show differentiation in the surface oxide film thickness. This *finding* is of great importance in further surface finishing investigations. It has been proven the magneto-electropolishing MEP to be an interesting means to achieve further modification of metal surface.

Consequently, it should result in better performance of titanium as a biomaterial. That means one may reduce the cross-section of the material to ensure the same performance, and *vice versa*. Our findings well confirm our early results concerning the effect of magnetoelectropolishing MEP and are in agreement with previous studies performed on CP titanium and other metallic biomaterials regarding their resistance to bending [3-7, 12].

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