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# NANOINDENTATION STUDIES OF TNZ AND Ti2448 BIOMATERIALS AFTER MAGNETOELECTROPOLISHING

## ABSTRACT

This work presents the nanoindentation results of two newly developed titanium alloy biomaterials, TNZ and Ti2448, after different surface treatments. The investigations were performed on the samples, AR – as received, MP – after abrasive polishing, EP – after a standard electropolshing, and MEP – after magnetoelectropolishing. The electropolishing processes, both EP and MEP, were conducted in the same proprietary electrolyte based on concentrated sulfuric acid. The mechanical properties of the titanium alloys biomaterials demonstrated an evident dependence on the surface treatment method, with MEP samples revealing extremely different behaviour and mechanical properties. Such a different mechanical behaviour may mean completely different composition and thickness of the surface film formed on the studied samples after MEP.

***Keywords:*** *Nanoindentation, magnetoelectropolishing MEP, TNZ surface, Ti2448 surface*

## INTRODUCTION

Titanium and its alloys are advanced metallic materials possessing many interesting features and properties with outstanding corrosion resistance in a wide variety of environments [1-12]. Because of numerous advantageous properties they are used in aeronautics, automotive industry, in the jewelry and biomedical engineering. CP Ti Grade 2 and NiTi alloys are known for years for their application as biomaterials. Other titanium alloys such as Ti–6Al–4V, Ti–6Al–4V ELI, Ti–6Al–7Nb have been used in prosthetic engineering [5,7-9] even if they contain carcinogenic vanadium and allergenic aluminum [5,13].

Our earlier studies indicated a considerable dependence of mechanical properties of titanium samples on the surface treatment method used [1,6,9-16]. It was proved the use of the magnetic field to the process of electropolishing resulted in a significant improvement of basic mechanical properties [1,12,16]. Some indentation and nanoindentation studies on stainless steels and titanium biomaterials were performed before [1,16,17] together with the significance of quantitative determination of material hardness stressed in the Authors' other work [14].

The two mechanical properties measured most frequently using indentation and nanoindentation techniques are the hardness *H*, or nanohardness *nH*, and the elastic modulus *E* [16-21]. The nanoindentation tests were used by the Authors before [1,17 ] to reveal the effect of magnetoelectropolishing MEP in comparison with the results obtained after a standard electropolishing EP technology [1,22]. The dependences, relationships and formulae on the depth of indentation, assuming isotropic materials, may be found in the related literature [1,18,23], with the reduced Young's modulus of the contact between the indenter and the sample $E_r$ determined by:

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

where *E* and *ν* are the elastic modulus and Poisson ratio for the sample, respectively, and $E_i$ and $\nu_i$ are the same quantities for the indenter. For the diamond indenter $E_i$ = 1141 GPa and $\nu_i$ = 0.07 [23].

The aim of the work is presenting changes in the mechanical properties of two new, important and advanced titanium biomaterial alloys. TNZ and Ti2448 biomaterials are focused [24]. In the studies, nanoindentation results obtained on the two titanium alloys after some definite heat treatments [24], named AR (as-received), then after abrasive mechanical polishing MP, and two finishing electrochemical operations, a standard electropolishing EP, and magnetoelectropolishing MEP, are presented.

## METHOD AND EXPERIMENTAL SET UP

### Sample preparation and SEM studies

For the nanoindentation studies, two new titanium biomaterial alloys TNZ and Ti2448 samples were used. Two sets of titanium alloys [25], TNZ and Ti2448 samples, of dimensions 30×20×2 mm were prepared. The composition of the samples is given in Table 1. Besides, the samples were:

- TNZ or Ti-20Nb-6Zr alloy was heat treated at 900 °C in a solution
- Ti2448 or Ti-24Nb-4Zr-7.9Sn alloy was heat treated at 300 °C, then water quenched for 3 minutes.

***Table 1.*** *Titanium TNZ and Ti2448 alloys' composition*

| TNZ of composition Ti-20Nb-6Zr [at%] | | | | |
|---|---|---|---|---|
| | Ti | Nb | Zr | |
| 1 | balance | 20 | 6 | |
| Ti 2448 of composition Ti-24Nb-4Zr-7.9Sn [wt%] | | | | |
| | Ti | Nb | Zr | Sn |
| 2 | balance | 24 | 4 | 7.9 |

Both sets of the samples were electrochemically treated, the first one under a standard electropolishing (EP) process, and the second one by electropolishing using a magnetic field (magnetoelectropolishing MEP) [1,22]. The electrolyte was based on concentrated $H_2SO_4$ with some addition of HF and $HNO_3$ acids. The same proprietary electrolyte was used both for EP and MEP processes under the same oxygen evolution regime, above plateau region. Afterwards the samples were washed out in a de-ionized water and dried in air. Such prepared samples were undergone to nanoindentation studies.

### Nanoindentation testing

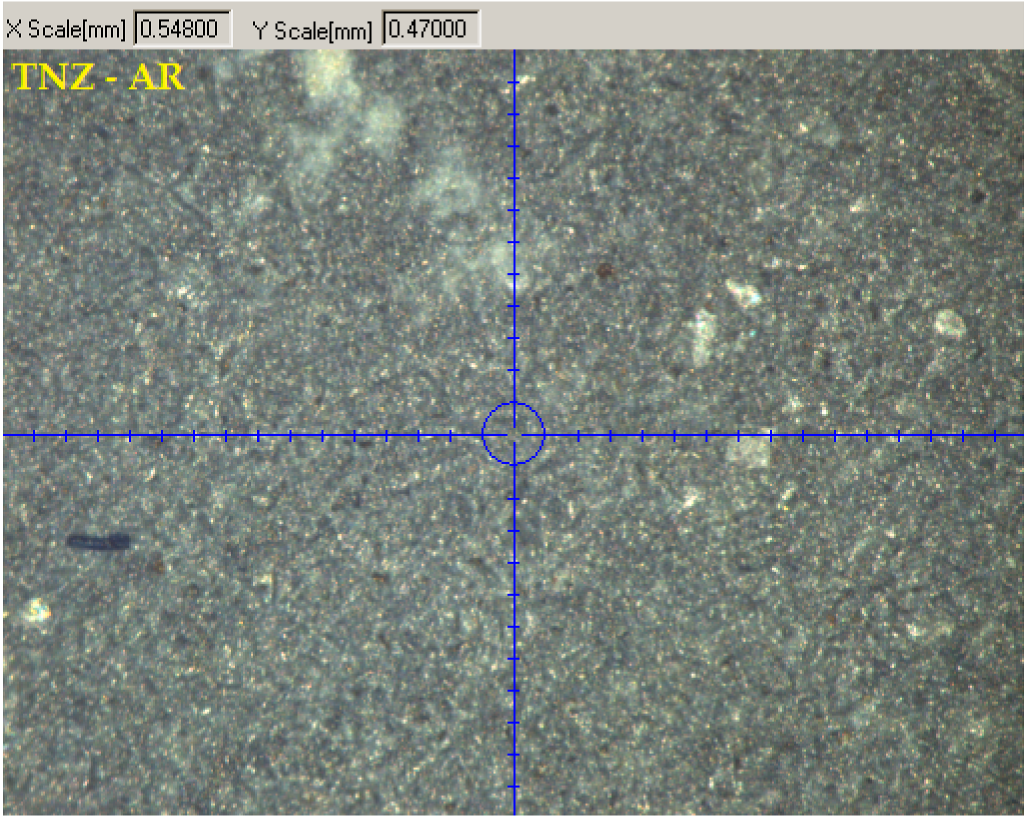
Nanoindentation measurements were performed on the 950 TriboIndenter™ Nanomechanical test instrument [23]. By using the instrument, quasistatic nanoindentation was applied to measure some mechanical properties such as Young's modulus, and nanohardness via nanoindentation. At least twelve imprints were taken each time on every sample investigated.

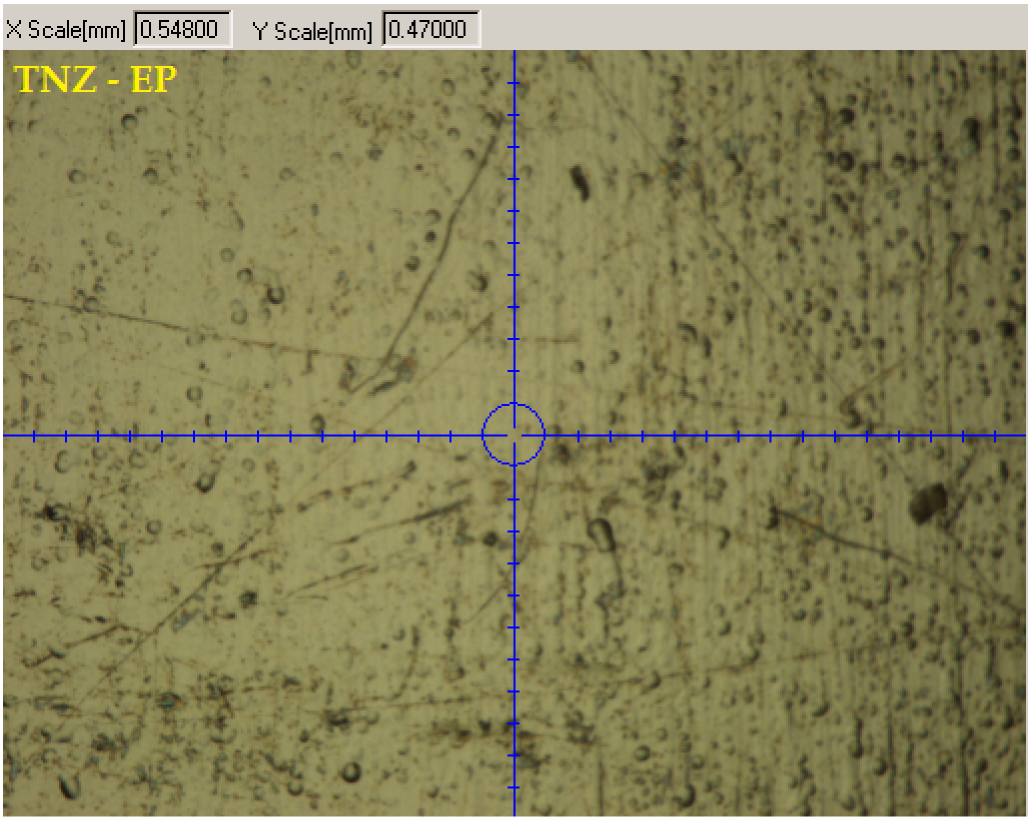
## RESULTS

Fig. 1 presents SEM results of TNZ alloy sample surface: AR – as received, EP – after electropolishing, MEP – after magnetoelectropolishing. By analogy, in **Fig. 2** the SEM results of Ti2448 alloy sample surface: AR – as received, EP – after electropolishing, MEP – after magnetoelectropolishing, are given. Although the composition of the two titanium alloy biomaterials are different, the AR surface (as-receved) looks amorphous. Abrasive polishing, using SiC grit size up to 1000, was used for both sets of samples prior to electrochemical treatments. Afterwards all samples, both TNZ and Ti2448 biomaterials, were polished electrolytically, in the first group by a standard electropolishing (EP), and in the second one – using magnetoelectropolishing MEP.

***Table 2.*** *Nanoindentation measurements results of TNZ and Ti2448 alloys' samples surface*

| TNZ | | | |
|---|---|---|---|
| | Contact Depth [nm] | Reduced Young's Modulus $E_r$ [GPa] | Nanohardness *nH* [GPa] |
| AR | 957.09 ± 355.21 | 3.61 ± 0.98 | 0.94± 0.48 |
| MP | 411.97 ± 166.59 | 89.19 ± 26.96 | 5.96 ± 2.26 |
| EP | 303.87 ± 28.79 | 83.08 ± 5.73 | 6.97 ± 0.92 |
| MEP | 280.67 ± 27.53 | 72.95 ± 7.21 | 7.64 ± 1.14 |
| Ti 2448 | | | |
| | Contact Depth [nm] | Reduced Young's Modulus $E_r$ [GPa] | Nanohardness *nH* [GPa] |
| AR | 295.90 ± 135.26 | 181.71 ± 60.41 | 9.17 ± 5.65 |
| MP | 333.64 ± 67.88 | 147.20 ± 29.73 | 7.32 ± 1.10 |
| EP | 264.95 ± 23.67 | 82.69 ± 6.32 | 8.26 ± 1.07 |
| MEP | 1040.12 ± 8.10 | 1.01 ± 0.01 | 0.59 ± 0.01 |


X Scale[mm] 0.54800
Y Scale[mm] 0.47000
TNZ - AR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Y Scale[mm] 0.47000
TNZ - EP

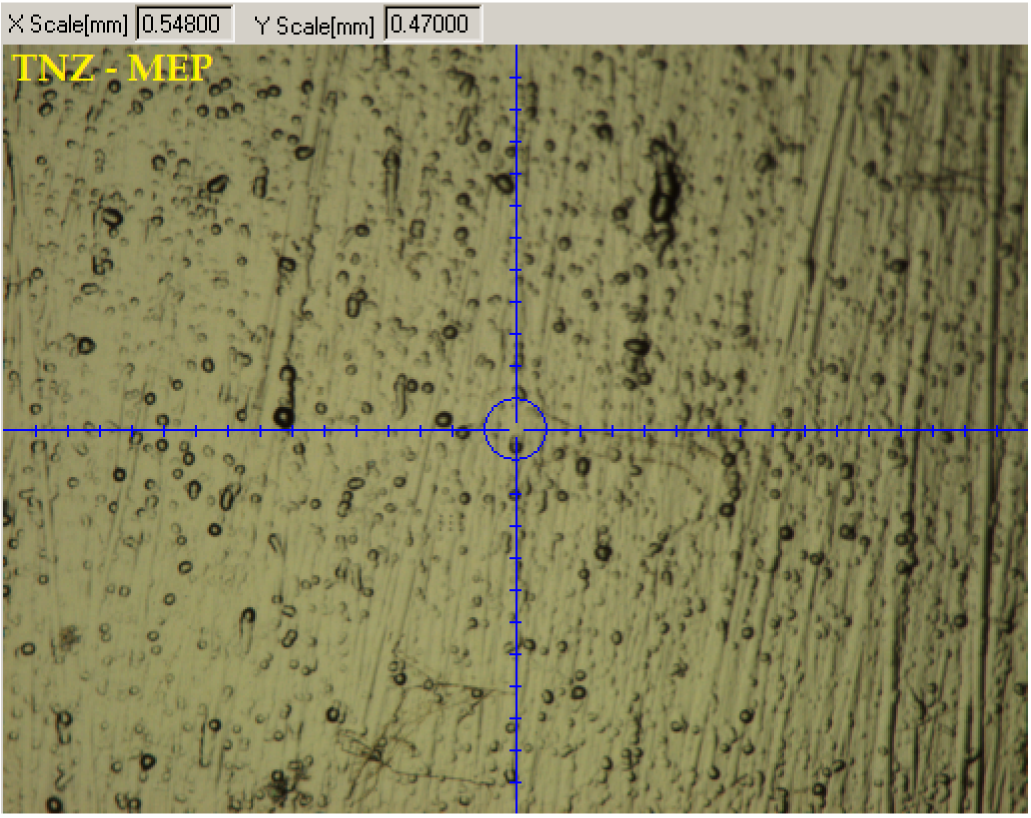
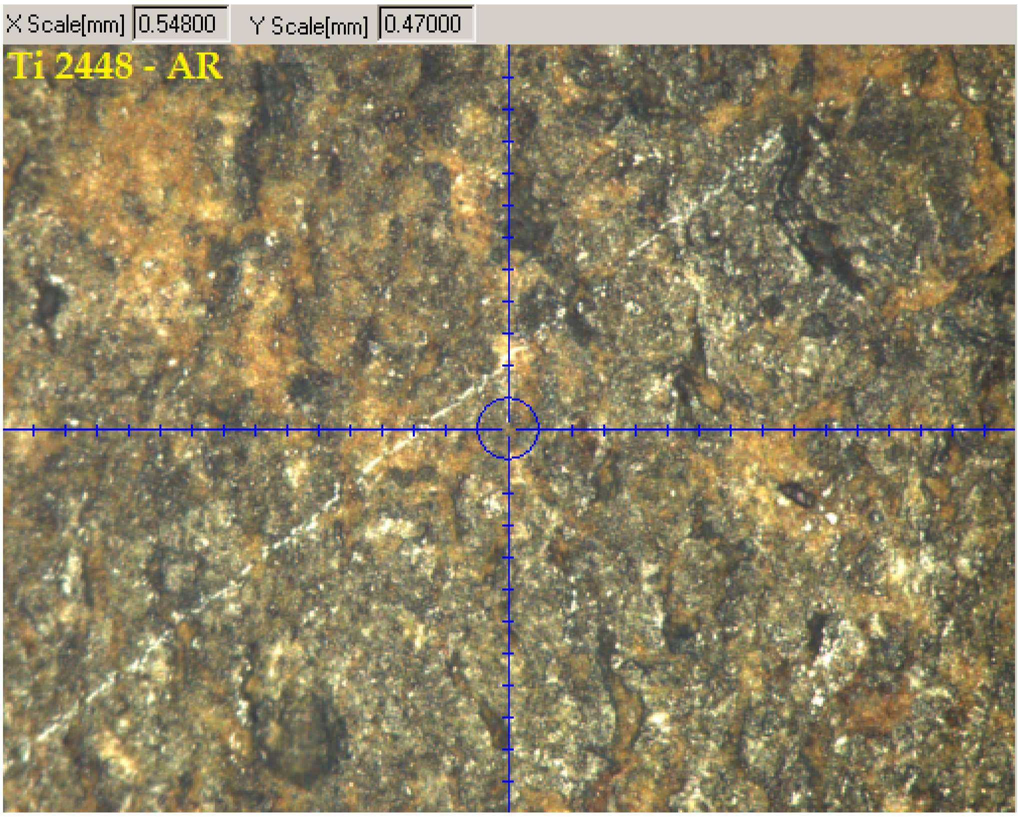



**Fig. 1.** SEM results of TNZ alloy sample surface: AR – as received, EP – after electropolishing, MEP – after magnetoelectropolishing



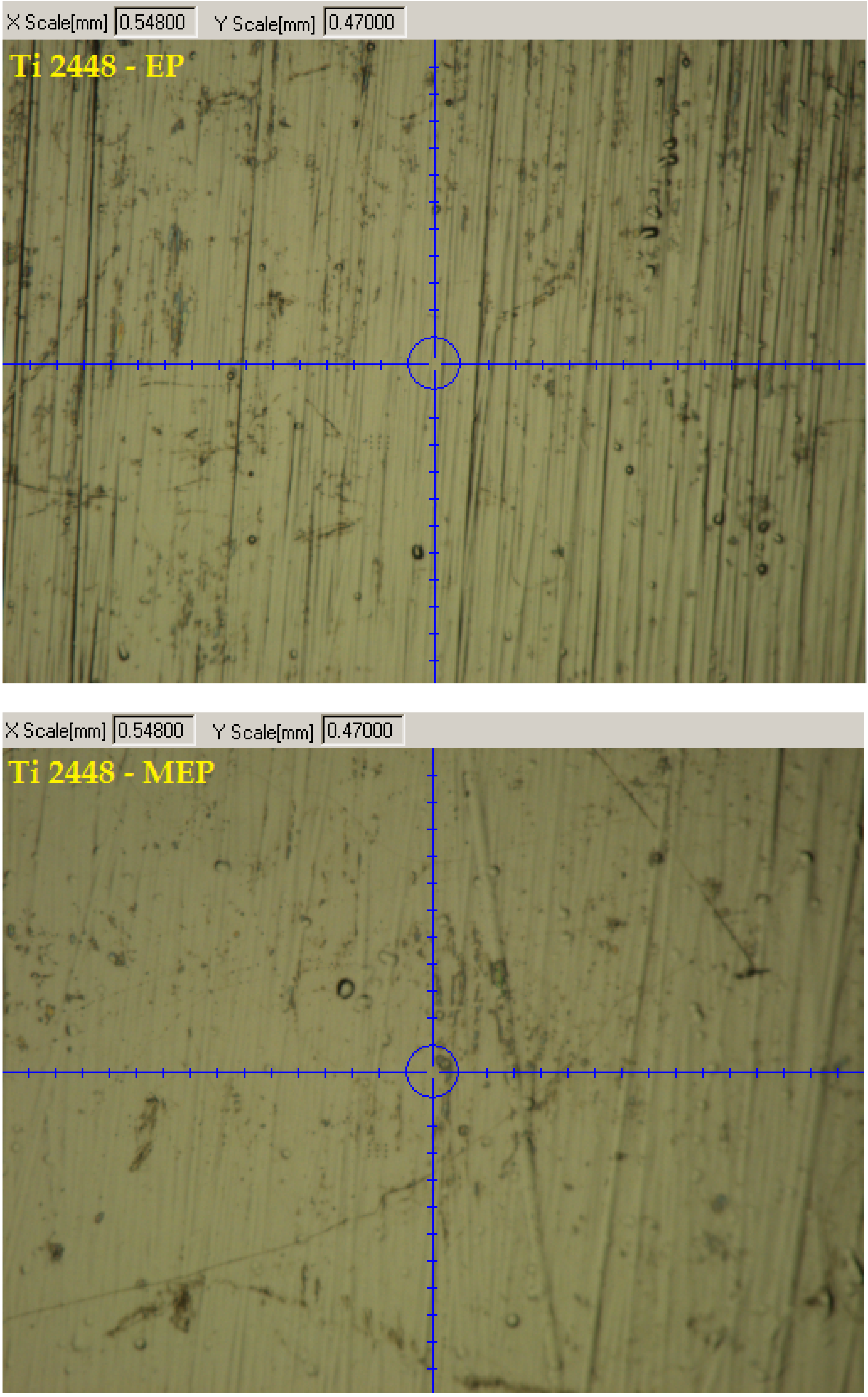
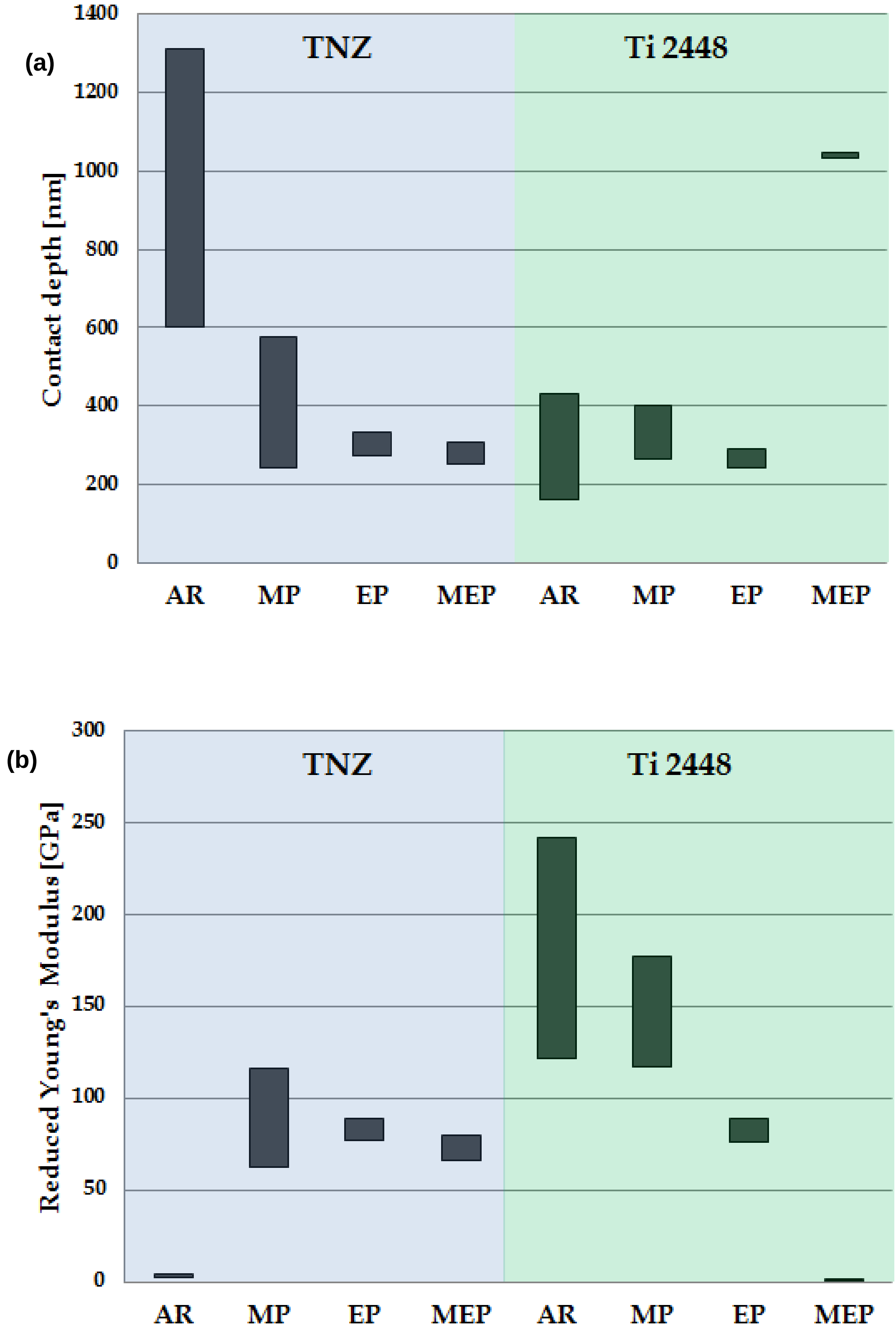



**Fig. 2.** SEM results of Ti2448 sample surface: AR – as received, EP – after electropolishing, MEP – after magnetoelectropolishing


(a)
TNZ
Ti 2448
Contact depth [nm]
1400
1200
1000
800
600
400
200
0
AR
MP
EP
MEP
AR
MP
EP
MEP
(b)
TNZ
Ti 2448
Reduced Young's Modulus [GPa]
300
250
200
150
100
50
0
AR
MP
EP
MEP
AR
MP
EP
MEP

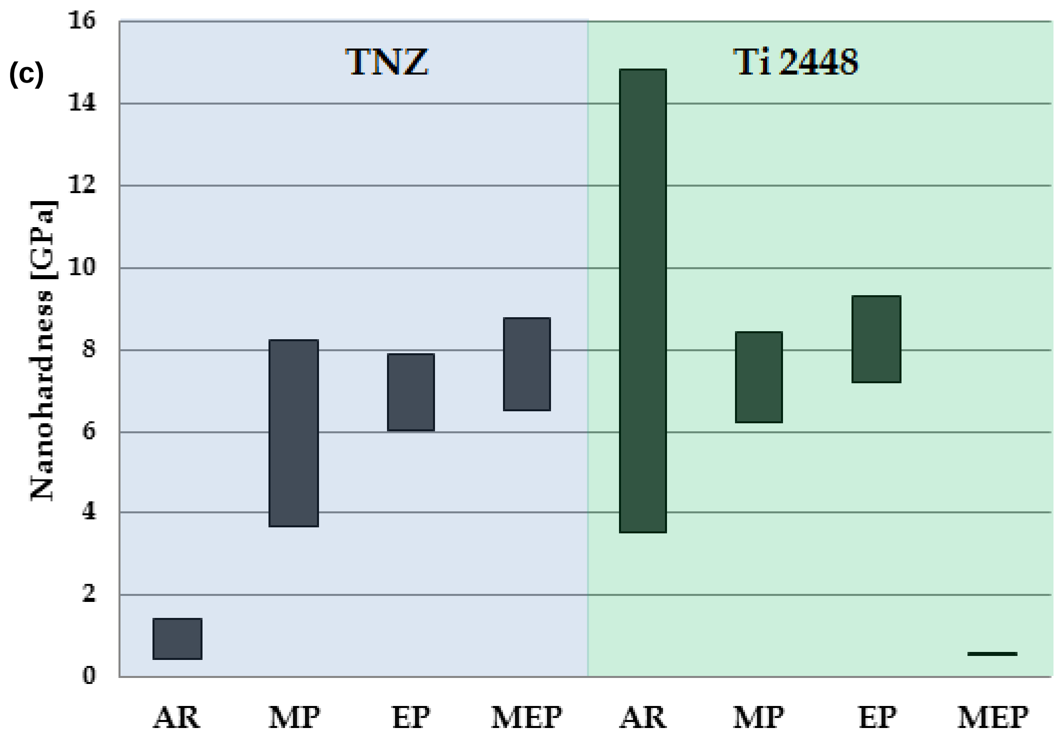



**Fig. 3.** Nanoindentation results of TNZ and Ti2448 alloy samples surface: (a) contact depth, (b) reduced Young's modulus $E_r$, and (c) nanohardness. For the horizontal axis description – see the text

Presentation of determination of the reduced Young's modulus and nanohardness of titanium alloy samples AR and those after MP, EP and MEP treatments are given in Table 2 and in Fig. 3. The nanoindentation mechanical data recorded for two titanium alloys TNZ and Ti2448 samples in four groups: AR, MP, EP, and MEP, vary concerning the madnitude and the range of changes. One may notice the differentiation in values of the contact depth, reduced Young's modulus and nanohardness obtained on the same biomaterial, TNZ and/or Ti2448, dependent on the state of material (AR) and method of the finishing treatment, referred to: MP, EP, and MEP.

Considering TNZ sample nanoindentation, the contact depth was decreasing from the highest value for AR sample, much over 900 nm, with the highest variability equaling ±355 nm, down to below 300 nm on MEP sample and about 13 times less variability, through MP and EP being in between. Thus the lowest reduced Young's modulus was found on AR sample, $E_r$ of about 3.60 GPa and the variability below ±1 GPa, but the highest on MP sample, about 90 GPa with very high variability of ±27 GPa, with some less value, 73 GPa on MEP sample. The nanohardness results are exactly reversal to the contact depth value, the lowest $nH$ = 0.95 GPa on AR sample with the variability below ±0.5 GPa, and the highest $nH$ = 7.64 GPa obtained on MEP sample and the variability some above ±1 GPa, with the MP and EP being in between.

Under Ti2448 sample nanoindentation, the least contact depth was obtained on EP sample, about 265 nm with some higher (about 296 nm) obtained on AR sample and with the highest variability, of about 135 nm. The highest contact depth was obtained on MEP sample, 1040 nm, though with the least variability, equaled about ±8 GPa; other contact depths were in between. The reduced Young's moduli are changing regularly from the highest obtained on AR sample (about 182 GPa), with the highest variability (over ±60 GPa), through the lesser values obtained on MP and EP samples, to the lowest (about 1 GPa), with the minimum variability equaling about ±0.01 GPa. The nanohardness study results followed reversal the contact depth values with the highest one, over 9 GPa and the biggest variability of ±5.65 GPa, down to the nanohardness equaling below 0.6 GPa with the minimum variability equaling about ±0.01 GPa; other two nanohardness values obtained on MP and EP samples were in between.

## DISCUSSION

Two electrochemical processes, EP and MEP, were used for the surface finishing of two newly developed titanium alloys, TNZ and Ti2448. The magnetic field was used in MEP to additionally modify the sample surface.

During these electrochemical processes, in the case of the TNZ (Ti–20Nb–6Zr) alloy, the reactions of the oxidation of its surface are as follows:

$$Ti + 2H_2O = TiO_2 + 4H^+ + 4e^-$$

$$2Nb + 5H_2O = Nb_2O_5 + 10H^+ + 10e^-$$

$$Zr + 2H_2O = ZrO_2 + 4H^+ + 4e^-$$

In case of the Ti 2448 (Ti-24Nb-4Zr-7.9Sn) alloy, apart from the higher mentioned ones, an additional reaction of oxidation will take place:

$$Sn + 2H_2O = SnO_2 + 4H^+ + 4e^-$$

Thus treated surfaces were scanned to reveal changes in the AR samples, after the EP, and MEP treatments (see Figs. 1, 2). Afterwards, basic mechanical properties were studied using nanoindentation procedure. The nanoindentation measurement results of titanium alloys TNZ and Ti2448 biomaterials were obtained on AR, MP, EP, and MEP samples, with the results presented in Table 2 and Fig. 3.

Table 2 covers mean values and standard deviations [25] presented graphically in Fig. 3. One may easily notice the comparison of the two studied titanium alloys shows the highest deviation in the contact depth on AR samples.

## CONCLUSIONS

The Young's modulus of elasticity and nanohardness of two titanium alloys, TNZ and Ti2448, were investigated using nanoindentation technique. The mechanical properties of the titanium alloys biomaterials demonstrated an evident dependence on the surface treatment method, in this the electropolishing parameters and conditions. After MEP treatment an improvement in Young's modulus of the same Ti alloy biomaterial is observed in comparison with the ones obtained after MP and a standard electropolishing (EP).

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

In fact it should result in better performance of titanium alloys as biomaterials. That means one may reduce the cross-section of the material to ensure the same performance, and *vice versa*. Our findings are in agreement with previous studies performed on CP titanium [1,6,9,10,17] and other metallic biomaterials regarding their resistance to bending [9,12,16,17].

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