Workshop on Biomaterials
BMAT 2005 – (pp.135–145) – Warsaw, 2005.

Evaluation of the Usefulness of Oxide Layer in the Intramedullary Nail Surfaces

Wojciech Chrzanowski

Institute of Material Science and Biomaterials
Silesian University of Technology
44-100 Gliwice, ul. Konarskiego 18a
wojciech.chrzanowski@polsl.pl

The problems of biomaterial selection and surface treatment can be solved nowadays on the basis of interdisciplinary considerations in the area of materials engineering, biomechanics and medicine. This kind of approach creates a chance to develop new implants or modify existing ones and obtain higher level of biocompatibility, bioactivity or inertness in the body [1–8]. The main purpose of the presented work was to evaluate the usefulness of the oxide layer used for improvement of intramedullary nail biotolerance. The layer was created by electrochemical treatment in newly developed baths. The evaluation was based on biomechanical test of the intramedullary nail, corrosion test and analysis of surface chemistry.

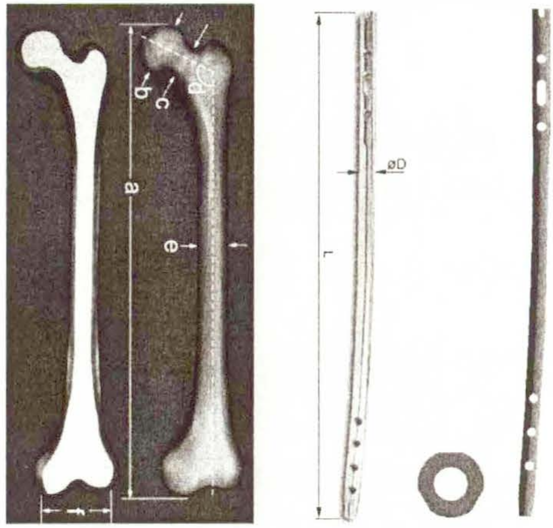
1. Methodology

1.1. Biomechanical Tests

1.1.1. Experimental method. The experimental test were carried out to determine the displacement and deformation in the femoral bone-intramedullary nail system.

In the experiment, the femoral bone model (Sawbone, Fig. 1a) and the intramedullary nail produced by BHH Mikromed (360×11) was used—Fig. 1b. To simulate a fracture of the bone it was cut in the middle. The fracture gap was 1 mm and it was sloping at an angle of 30° to the vertical axis of the bone. The bone was integrated using the intramedullary lock nail made of stainless steel [1, 4]. The mechanical properties were as follows:

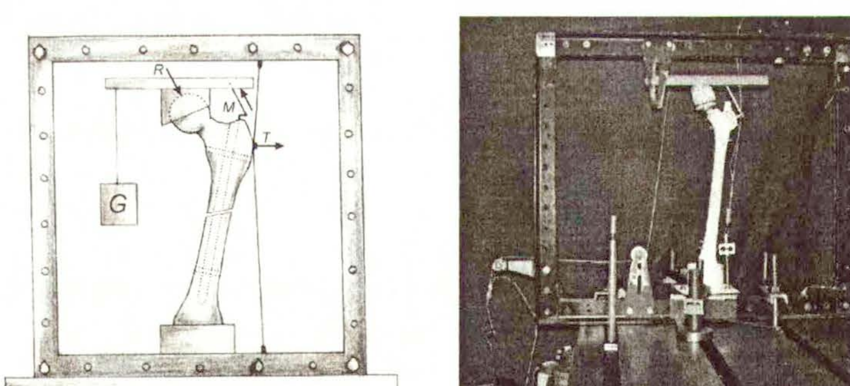
- $E_{\text{bone}} = 18600\,\text{MPa}$, $\nu = 0.3$,
- $E_{\text{steel}} = 200000\,\text{MPa}$, $\nu = 0.33$.



(a) (b)

FIGURE 1. a) the bone model used in the research, b) the nail used in the research

A dedicated stand was built—Fig. 2. The stand enables application of three groups of forces: R—reaction on the femoral head, M—reaction of gluteus muscle and T—reaction of tractus iliotibilais—Fig. 2. The Speckle Interferometry Method was used to determine the displacement of the points



(a) (b)

FIGURE 2. The test stand used in the experimental examination

located on the bone axis [9]. In the test, the increase of the load between two expositions was 20 N.

Additionally, a similar experiment was carried out using the dial gauges, to check if the results are linearly dependent on the load rise. Four gauges were placed along the bone and load up to $G = 40\,\mathrm{kg}$ was used.

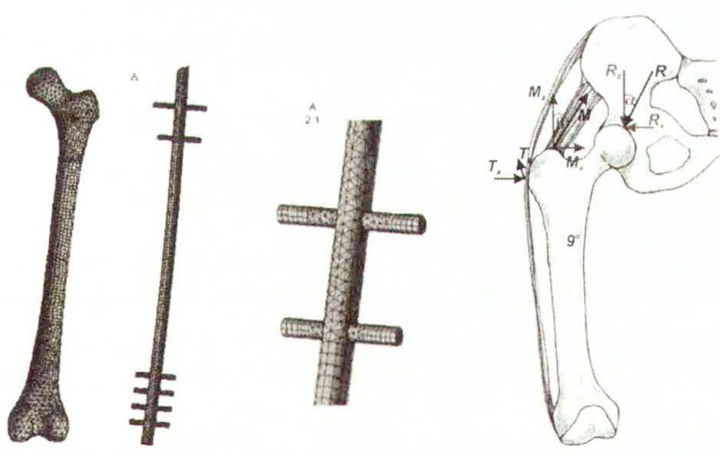
1.1.2. Numerical analysis. The numerical analysis was carried out to verify results obtained in the experimental test and also to determine stress and strain state in the nail.

The numerical model of the femoral bone-intramedullary nail system was worked out on the basis of geometrical model of femoral bone, which was created in Institute of Rizzoli [10] and on the basis of geometry of the nail used in the experiment. The analysis was carried out for two sets of material properties of the nail (stainless steel and titanium alloy) [3, 4, 11]:

- $E_{\mathrm{ss}} = 200\,000\,\mathrm{MPa}$, $\nu = 0.33$,
- $E_{\mathrm{Ti}} = 110\,000\,\mathrm{MPa}$, $\nu = 0.33$.

Titanium alloy was chosen as a one of the most popular materials used for orthopaedic implants.

In the analysis loading scheme shown in Fig. 3. was applied. The force values were equal to the values used in the experiment. It enabled us to com-



(a) (b)

FIGURE 3. a) numerical models of the bone and the nail, b) the loading scheme used in the numerical analysis

pare the results of both experimental and numerical tests. In the next stage, the displacement of the model elements were evaluated for the phase of walking associated with highest values of loading. The forces were calculated for the person who weights 70 kg—see Table 1. These displacements are crucial to assess the maximum deformation of the nail which is important for the testing procedure of the implant materials and the surface layer.

TABLE 1. The components of loads

R_x N	R_y N	R_z N	M_x N	M_y N	M_z N	T_x N	T_y N	T_z N
494	0	1824	−494	0	1208	−54	−21	0

1.2. Specimen Preparation

In continuation of this research a titanium alloy Ti6Al4V ELI was chosen due to its good mechanical and chemical properties [2–4]. For this material a procedure of surface preparation was proposed. It included the following steps:

- grinding,
- electropolishing and,
- anodic oxidation.

In the research, the bars of circular cross-section (diameter 7 mm) were used as specimens. Electropolishing was carried out in newly developed bath composed of hydrofluoric acid+sulphuric acid+glycol+acetanilide. Anodic oxidation was done in chromic acid [3, 12, 13, 14].

1.3. Surface Examinations

One of the factors that influence the usefulness of the surface treatment is roughness. For short term implants, it is admitted in principle that parameter R_a should be below 0.16 μm [4]. In the investigation profilographometer Surtronik 5+ was used to assess R_a parameter after every step of surface preparation.

To assess the influence of the electrochemical treatment on corrosion resistance a potentiodynamic investigation in the Tyrode's solution ($36.6\pm1°$C and pH=7.5–8.4) was carried out.

It is very important to check if the layer is flexible because the implant is deformed during its life, as was shown in the biomechanical tests. To assess the flexibility of the oxide layer extra potentiodynamic tests were carried out for deformed (angle 10°, 20°, 45° and 90°) specimens. The angle of 10° was measured between the directions of the nail axis corresponding to the biomechanical tests in two situations—for zero and maximum load applied to the bone. Testing for higher angles was done to check the layer flexibility in harsh conditions.

The chemistry of the modified surface was evaluated using the XPS method.

2. Results

2.1. Biomechanical Test Results

2.1.1. Experimental test results. The analysis of the speckle pictures showed that the maximum displacement (in the frontal plane) of the bone together with the nail, for the force increment $\Delta F = 20$ N was $dx_{\max} = 0.569$ mm, and occurred in the top part of the bone—Fig. 4.

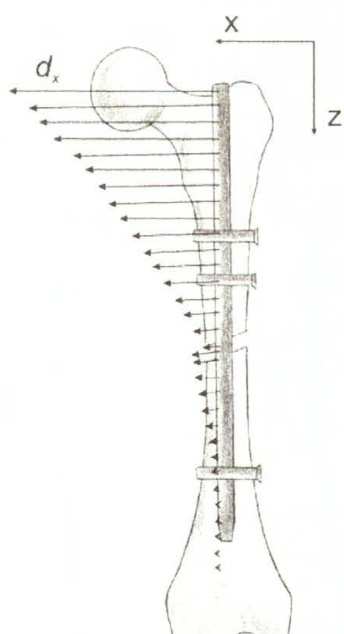


FIGURE 4. The displacements along the model obtain from the Speckle Interferometry analysis

Additionally, the experiment in which dial gauges were used showed that there is linear dependence between force and displacements of the analyzed system and the precise results obtained from the Speckle Interferometry method can be transferred to other force increment value.

2.1.2. Numerical analysis results. The Finite Element Method enabled us to assess displacements and stress distribution in the bone, the nail and in the assembled model.

The maximum displacement of the whole model occurred, like in the experimental model, in the top part of the model and it was $Dx_{\max} = 0.575$. A high correlation between the results of both the experimental and the numerical methods was observed.

The maximum displacements of the top part of the model, for the phase of walking, with the highest values of forces were for $D_{\max\mathrm{SS}} = 26.6\,\mathrm{mm}$ and $D_{\max\mathrm{Ti}} = 32.1\,\mathrm{mm}$ respectively for the stainless steel and titanium alloy nail—Fig. 5a, c. These displacement values corresponded to the nail bend 5° and 6°. This is important for selection of surface layers that are continuous, flexible and do not crack when the implant is deformed.

Additionally, the stresses distribution was obtained in the numerical analysis. It was noted that, generally, in the nails the von Mises stress did not exceed 580 MPa (for the steel) and 590 MPa (for the titanium alloy).

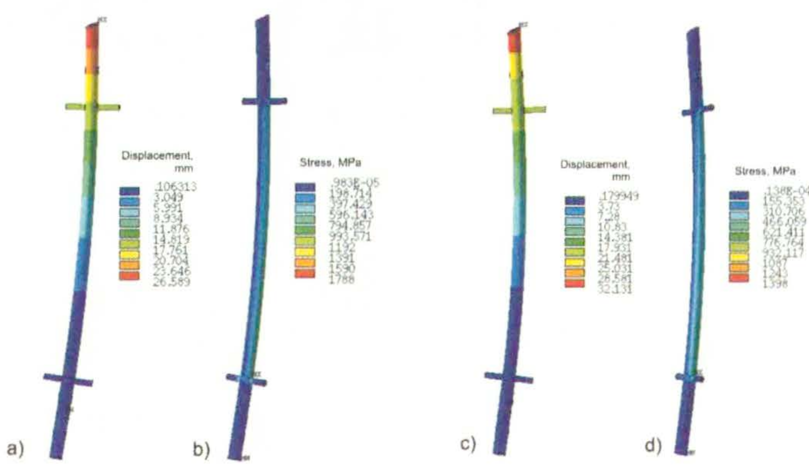


Figure 5. Displacement and stress distribution in: a, b) the stainless steel nail, c, d) the titanium alloy nail

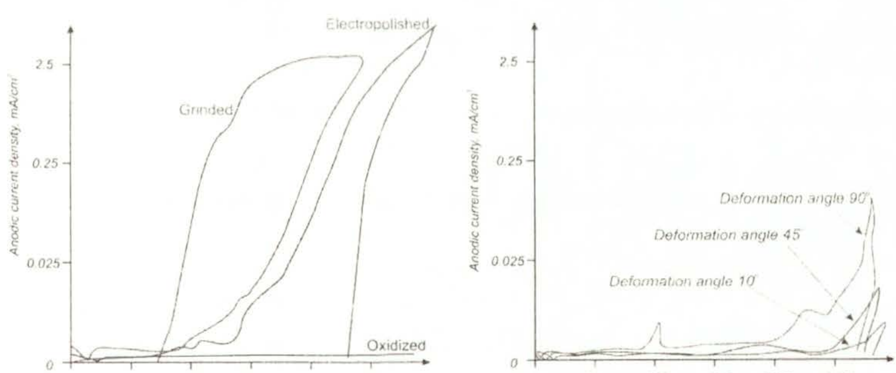
Only locally, in the area surrounding the holes for locks, stresses increased to 1788 MPa and 1398 MPa respectively for the steel and titanium alloy—Fig. 5b, d.

2.2. Surface Topography and Electrochemical Test Results

A roughness of the grinded surface of Ti6Al4V ELI specimens was in the range $R_a = 0.78$–$0.85\,\mu$m. The electropolishing and anodic oxidation, in newly developed baths, caused decrease of the surface roughness—$R_a = 0.10$–$0.14\,\mu$m.

The results of the potentiodynamic examination were collected in Table 2. Ti6Al4V ELI alloy with grinded surface had the corrosion potential in the range of $E_{cor} = 50$–59 mV, the transpassivity potential was in the range of $E_{TP} = 1540$–1980 mV. Electrochemical polishing caused 75 mV increase of the corrosion potential E_{cor} and 500 mV increase of transpassivity potential E_{TP}. For the electrochemically polished and oxidized specimens the corrosion potential increased to $E_{cor} = 342$–402 mV. A significant increase of anodic current density in the range up to +5V was not observed for the oxidized specimens—Fig. 6a.

In the group of the deformed specimens slight decrease of corrosion resistance was observed. The corrosion potential fall to $E_{cor} = 211$–273 mV was



(a) (b)

Figure 6. a) Anodic polarization curves for Ti6Al4V ELI specimens with grinded, electropolished and oxidized surfaces, b) potentiodynamic curves for Ti6Al4V ELI specimens with oxide film, at different deformation angles

observed for the specimens deformed to about 10°. The transpassivatity potential was in the range of $E_B = 4710$–4920 mV. Increasing the deformation angle to 45° causes further decrease of the corrosion and transpassivity potentials to value $E_{cor} = 70$–78 mV and $E_{TP} = 4300$–4918 mV. For the deformation angle 90° the potentials were: $E_{cor} = 25$–35, $E_{TP} = 3750$–4280 mV—see Table 2, Fig. 6b.

TABLE 2. The results of potentiodynamic tests

Specimens	**Deformation angle °**	**Corrosion potential** E_{corr}, mV	**Transpassivity potential** E_{TP}, mV
Grinding	N/A	$+50 \div +59$	$+1540 \div +1980$
Electropolishing	N/A	$+112 \div +125$	$+2270 \div +2310$
Electropolishing+ anodic oxidation	N/A	$309 \div 409$	>5000
Electropolishing+ anodic oxidation	10°	$+211 \div +273$	$+4710 \div +4920$
	45°	$+70 \div +78$	$+4300 \div +4918$
	90°	$+25 \div +35$	$+3750 \div +4280$

A current density in the passive range of the deformed specimens was similar to the current noted for undeformed, oxidized specimens and lower than for grinded and polished specimens. Little changes of the potentiodynamic curve shapes did not indicate impairment of the layer.

The chemistry of the modified surface was evaluated using the XPS method. The layer was composed mainly of titanium, aluminum and vanadium oxides (TiO_2, Al_2O_3, V_2O_5) and small quantity of other alloy compounds, contaminants from the air and the chemical baths—Table 3, Fig. 7.

TABLE 3. Chemical composition of oxide layers on the titanium alloy—XPS examinations

Elements	O	Ti	Al	V	F	N
Atomic concentration %	41.29	9.29	2.08	0.33	1.68	2.03
Chemical compound	TiO_2+ contamination	TiO_2	Al_2O_3	V_2O_5	Ca_2F	–
Elements	C	Cr	S	Na	Ca	K
Atomic concentration %	37.17	2.15	0.48	1.30	0.56	1.01
Chemical compound	contamination	Cr^{3+}	sulfates	–	Ca_2F	–

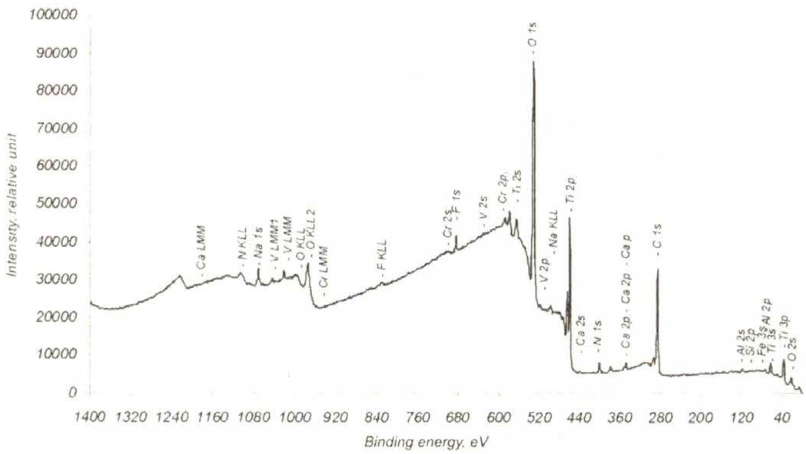


FIGURE 7. The survey spectrum of the polished and oxidized Ti6Al4V ELI specimen

The concentration of the aluminum and vanadium in the layer was lower than in the bulk material. This can be recognized as favorable due to the toxic reaction of these elements in the body.

3. Discussion

The displacements distribution of the femoral bone-intramedullary nail model during the loads bearing was assessed in the biomechanical tests. It was shown that the deformation angles for the nails made of stainless steel and titanium alloy did not exceeded 6°. Additionally, the stress distribution was investigated. The maximum stress value for extreme conditions (the phase of walking when the whole body weight is supported by one leg) exceeded in some places the tensile strength of the materials. It came out in this analysis that just after the nail implantation the patient should not put his full weight on his leg.

For the implant made of titanium alloy (Ti6Al4V ELI) the electropolishing and anodic oxidation in newly developed baths was carried out. These treatments ensure a roughness $R_a \leq 0.16\,\mu$m required for these kinds of implants and also caused an increase of corrosion resistance. Additionally, on the basis of recorded anodic polarization curves for the specimens which were deformed in the range of $0^{\circ} \div 90^{\circ}$, the flexibility of oxide layers was assessed. Slight changes of the anodic polarization curves shape with increase of deformation angle were observed. It indicated that the layer is flexible due to insignificant variations of anodic current density in the passive area for deformed and undeformed specimens. A wide passive range was also noted. It showed that deformation did not cause destruction of the layer. The chemistry of the modified surface was evaluated using the XPS method. The layer was composed mainly of titanium, aluminum and vanadium oxides (TiO_2, Al_2O_3, V_2O_5) and a small quantity of other alloy compounds, contaminants from the air and the chemical baths. The concentration of the aluminum and vanadium in the layer was lower than in the bulk material. This can be recognized as favorable due to the toxic reaction of these elements in the body [4].

As a result of the research it can be stated that the oxide layer created using newly developed methods, increases corrosion resistance. The flexibility of oxide layer is satisfactory in applications for surface modifications of the intramedullary nail. In order to evaluate the tribological properties of the layer, tribo tests are planned in the future.

Acknowledgement

The author would like to acknowledge the help and support of Prof. Romuald Będziński, Dr. Ludomir J. Jankowski, Dr. Ginter Nawrat, Prof. Jacek Szade, Dr. Antoni Winiarski, BHH Mikromed.

Financial support from State Committee for Scientific Research, 4T08C 04122 is gratefully acknowledged.

References

1. I. KEMPF and K.S. LEUNG, *Practice of Intramedullary Locked Nails, Scientific Basis and Standard Techniques*, Springer-Verlag, Berlin Heidelberg 2002.
2. X. LIU, P.K. CHU, and CH. DING, *Surface modification of titanium, titanium alloys, and related materials for biomedical applications*, Materials Science and Engineering R47 : 49–121, 2004.
3. D.M. BRUNETTE, P. TENGVALL, M. TEXTOR, and P. THOMSEN, *Titanium in Medicine*, Springer-Verlag, Berlin Heidelberg 2001.
4. J. MARINIAK, *Biomateriały*, Wydawnictwo Politechniki Śląskiej, Gliwice 2002.
5. A.E. GOODSHIP and J. KENWRIGHT, *Controlled mechanical stimulaton in the treatment of tibial fractures*, Clinical Biomechanics, **241** : 36–47, 1989.

6. S. Wolf, A. Janousek, W. Veith, F. Haas, D. Duda, and L. Cleas, *The effects of external mechanical stimulation on the healing of diaphyseal fixed by flexible external fixation*, Clinical Biomechanics, **13** : 359–364, 1988.

7. X. Zhu, K-H. Kim, and Y. Leong, *Anodic oxide films containing Ca and P of titanium biomaterial*, Biomaterials **22** : 2199–2206, 2001.

8. B. Groessner-Schreiber and R.S. Tuan, *Enhanced extracellular matrix production and mineralizaion by osteoblasts cultured on titanium surface in vitro*, J. Cell. Sci., **101** : 209–217, 1992.

9. R. Będziński, *Biomechanika inżynierska* [in Polish], (Engineering Biomechanics), Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 1997.

10. *The ISB Finite Element Repository*, Istituti Rizzoli, www.cineca.it/hosted/LTM/back2net/ISB_mesh/, 1997.

11. PN EN-ISO 5832

12. J. Lausmaa, *Surface spectroscopic characterization of titanium implant materials*, Journal of Electron Spectroscopy and Related Phenomena, **81** : 343–361, 1996.

13. J. Lausmaa, B. Kasemo, H. Mattsson, and H. Odelius, *Multi-technique characterization of oxide films on electropolished and anodically oxidized titanium*, Applied Surface Science, **45** : 189–200, 1990.

14. *Patent* FR 2795433, WO0100906, AU 6449700, US6610194, Cn 1358240T, EP 1194617, GB 2060700

Already appeared in the ABIOMED *Lecture Notes* series:

1. J. MIZRAHI, *Muscle/Bone Interactions in the Musculo-Skeletal System*
2. A. NOWICKI and J. LITNIEWSKI (Eds.), *Proceedings of the Workshop on Ultrasound in Biomeasurements, Diagnostics and Therapy*
3. J. PIEKARSKI (Ed.), *Tissue Remodelling*
4. S. SIDEMAN, *Insight into the Heart: Cardiac Energetics*