

EXPERIMENTAL RESEARCH OF THE DURABILITY AND WEARING OF UHMWPE WITH DIFFERENT COATINGS

ABSTRACT

In the paper there are discussed artificial hip joint components, materials, UHMWPE with different coatings (Co+TiO₂, Co-Cr-Mo, Zr and ZrO₂) and magnetron sputtering method, which is used to coat UHMWPE. The coatings microstructure research before and after the friction test has been done. During the research, 15 % of polyvinylpyrrolidone has been used as an artificial joint lubricant and the friction test has been carried out in vertical plane and UHMWPE samples were rubbed at the same working conditions. It has been determined that after the friction test Co+TiO₂ coating has shown the best endurance and the greatest abrasion resistance.

Keywords: coating, scanning probe microscope, durability

1. INTRODUCTION

Development of replacement arthroplasty touched a number of problems. These problems include the design of the implanted components, a way of their fixation, properties, rubbing surfaces and their wear resistance [1, 2, 3]. In scientific publications of the last decade the consequences of the wear of articular surfaces, such as osteolysis and survival of mechanical fixing components, are frequently discussed [1,4]. Osteolysis is understood as a bone resorption or the massive formation of cystic granuloma around an implant [1, 4, 11]. The bone resorption around the implanted hip joint components is one of topicalities of today's surgical replacement arthroplasty that predetermines the service life of the mechanical fixtures of the implanted components [4].

For manufacturing the components of an artificial hip joint various materials are used; they include metals and their alloys (titanium and its oxides, stainless steel, cobalt-chromium-molybdenum alloy) [2, 3, 5], ceramics (aluminum oxide, zirconia) [6, 7, 8] and polymeric materials (PMMA, UHMWPE) [5, 9, 10].

Polymeric materials used in the production of the implants have become abundant; however, for over 40 years, Ultra-High Molecular Weight Polyethylene (UHMWPE) is used in the production of hip joint endoprotheses [5]. The said material is used for producing the insert of the hip joint socket [5, 6]. It is distinguished for its low friction coefficient, good biocompatibility and lubricant properties; however, its break fracture resistance is lower, leading it to rapid wear. In addition, particles of worn polyethylene get into the body and cause the undesirable reaction of the tissues, known as osteolysis [4, 11]. In such case, the patient becomes a subject for the revision surgery of the hip joint replacement arthroplasty.

At present, the modification of metal or plastic surfaces of the implants is very often analysed [12, 13]. The modification of a polymer surface, either by chemical or physical methods, is very important in order to achieve its new uses and different properties.

Comment [E1]: Shall be «its».

Comment [E2]: Analyzed

Comment [E3]: Shall be «its».

This is especially true when referred to inert polymers, as is the case of polyethylene, whose surface needs etching treatments to improve their biocompatibility and their adhesion via printing or decoration finishes [9, 10, 11].

The previous researches have shown that when the elastic module of the material of hip endoprosthesis socket is low and the stiffness of femoral stem is high, the pressure in contact surfaces is reduced considerably, lubrication conditions are improved and the durability of hip endoprosthesis is increased [14]. The researches have shown that when coating the polyethylene surface of the socket with durable TiO₂ and Co-Cr-Mo coatings, on one side the surface contact is hardened but on the other side it is coated on a resilient base and this allows it to increase the surface contact [15]. Such solution helps reduce stresses and considerably improve the wear-and-tear resistance. The above combination can be applied in the fields where it is crucial to extend service life of frictional parts and units that are featured for their restricted lubrication properties undertaking damping of vibrations and impacts.

UHMWPE is coated with different coatings to improve its mechanical properties & durability and to reduce its wear herewith the number of fragments that cause host reaction to the artificial hip joint [15]. However, only primary tests on durability of the said coatings were carried out in the above-mentioned works as of 2500 friction cycles only. This number is too low because the joints on their movement are subjected to considerably higher number of cycles. In addition, various coatings, for instance, zirconium and zirconia can be used. Zirconium is distinguished for its good biocompatibility properties and its elastic module is close to the elastic module of human bones. Zirconia is highly biocompatible, as are other ceramics, and can be made in the form of large implants such as the femoral head and acetabular cup in total hip joint replacement [16]. In the present research, the coatings of UHMWPE (Chirulen (ISO5834-2, from POLY Hi Solidur MediTECH company)) with zirconium, zirconia, titanium oxide and cobalt-chromium-molybdenum alloy were applied to carry out friction tests on a stand, to examine the microstructure of the coatings by a scanning probe microscope (SPM) before and after the friction tests to identify what coating withstood 10 000 working cycles in the best way.

Magnetron sputtering method was chosen, since the application of coatings takes place at 70°C, and by the application of this method properties of polyethylene do not change (its melting temperature varies between 144 °C and 152 °C). Magnetron sputtering technology is characterized in this way: oxide coatings which can be sputtered (reactive sputtering), excellent layer uniformity, very smooth sputtered coatings (no droplets). Magnetron sputtering technology has some disadvantages: slow deposition speed and the adhesion of coatings is lower and the density of the sputtered layers may be lower [15].

2. MATERIALS AND METHODS

For the formation of the coatings, 3-source magnetron sputtering SCM was used. Coatings were made with such parameters of the system: Ar⁺ ion flow 20 cm³/min; operating pressure 0.6 Pa; deposition time t = 60 min; current strength I = 0.8 A; voltage U = 270 V. Distance between magnetron and substrate 270±2 mm. Three specimens prepared for each coating group (Co-Cr-Mo, Co+TiO₂, Zr and ZrO₂).

The surface of samples has been measured by scanning probe microscope (SPM) (Dimension 3100, Digital Instruments, USA). The instrument operates under atmospheric pressure at room temperature (20-22°C) and works in air. Samples' diameter is 10 mm, height is 7 mm. The SPM is equipped with an in-line optical zoom microscope with color CCD camera, with a maximum magnification of 800x for precise placement of the SPM

Comment [E4]: Shall be «its».

Comment [E5]: Shall be «its».

Comment [E6]: Shall be «its».

Comment [E7]: UHMWPE (Chirulen (ISO5834-2, POLY Hi Solidur MediTECH, Company))

Comment [E8]: Must be in the Discussion part

probe onto the sample. Measurements include surface roughness and particle size, with a noise floor in height measurement of 0.02 nm.

Coatings have been tested for their abrasion resistance and durability. For this purpose a special rubbing device generating friction effect has been designed and manufactured (Fig. 1).

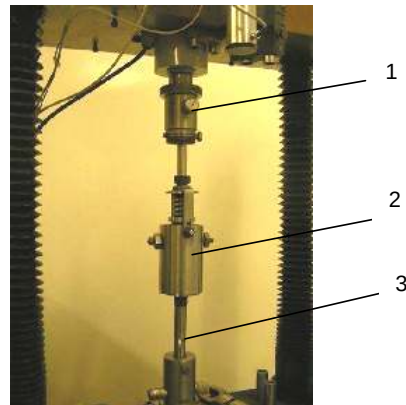


Figure 1. Device and its parts: 1– FP-10 tensioning equipment; 2 – special device; 3 – rod

The device for the stand is intended for operation in the FP-10 tensioning equipment (Heckert, Germany). The stand is used for simulation of real movements taking place in the human hip joints. One cycle is back-and-forth motion of the stand's rod 3. Within such cycle, a sample inserted in the fixture 2 is loaded from 0 to the maximum force (400 N) and it is rotated at a certain angle (-2° - $+2^{\circ}$). Within one cycle, the sample performs a complex movement, i.e. it is pressed and rotated, thus simulating motions and loads of a hip joint. For lubricating, 15 % polyvinylpyrrolidone was used. During durability and wearing tests, 10 000 cycles were applied upon the load of 400 N. The testing has been accomplished at room temperature. Each test has been repeated three times. The analysis of variance has been used for statistical evaluation of the test results.

After the wearing tests, the microstructure of the coatings was examined again by a scanning probe microscope. Finally, the analysis of the obtained results was carried out. The coating which has changed little or hasn't changed at all after the friction test has had the highest abrasion resistance.

3. RESULTS AND DISCUSSION

The results of the tests are provided in Figs 2 and 3. In Fig. 2 the photos of the microstructure of Co+TiO₂, Co-Cr-Mo, Zr and ZrO₂ coatings applied onto UHMWPE by magnetron sputtering are provided; they were made by a scanning probe microscope before friction tests. In the course of the analysis of SPM surface morphology images (Fig. 2), it was found that the largest agglomerates of granules are formed in Co-Cr-Mo coating (about 2 μ m long, 7 μ m wide and 10 nm high). The roughness of Zr coating is the minimum; however, it includes large agglomerates of granules (1.5 $\times$ 1.7 μ m). Zirconium is known as a crystal

structure comminuting agent and shows particularly good granular structure refinement effect. The roughness of ZrO_2 coating is relatively low ($3.2 \times 2.5 \mu\text{m}$); however, the structure of the coating consists of large granules. $\text{Co}+\text{TiO}_2$ coating is of a moderate roughness with $4.5 \times 4.5 \mu\text{m}$ granular agglomerates.

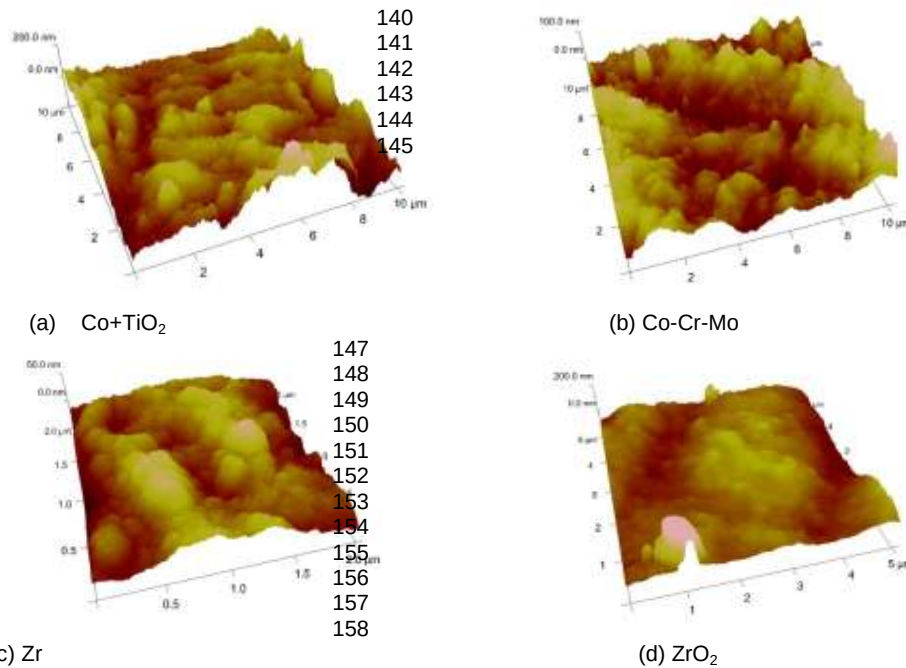


Figure 2. SPM surface morphology images before friction test for the coatings; (a) $\text{Co}+\text{TiO}_2$, (b) Co-Cr-Mo , (c) Zr , and (d) ZrO_2

It was found that after coating with $\text{Co}+\text{TiO}_2$ the sizes of particles were found to be between 50 nm and 200 nm, creating a rough surface. The average sizes of particles are provided in Table 1.

Coatings			
$\text{Co}+\text{TiO}_2$	Co-Cr-Mo	Zr	ZrO_2
Mean values $\pm$ SDs			
135,9 $\pm$ 63,13	58,66 $\pm$ 34,19	34,13 $\pm$ 18,43	164,96 $\pm$ 54,13

Table 1. The average mean values of particles sizes (nm). Data are given in Mean $\pm$ SD.

On the analysis of the SPM surface morphology images after the tests on friction stand, it was found that $\text{Co}+\text{TiO}_2$ coating was distinguished for the best mechanical properties, because the changes of its grain and the shape of its granules particles were inconsiderable.

Comment [E9]: Granular agglomerates???

Comment [E10]: This should be replaced by a figure with bars, showing the statistical differences between the bars with «*» showing related p value. This shall also be done for Table 2.

The t-test showed that before and after the friction tests a certain statistical difference between the coatings was calculated ($p < \alpha = 0.05$). Co-TiO₂ mean values of particles size $\pm$ SD after the friction tests has altered the least. ZrO₂ showed the worst mechanical properties: it can be seen from the SPM photo that the surface of this material wore to the maximum extent and residue on UHMWPE was the smallest. After the friction tests, the grain and roughness of the above-described Zr coating increased and the shape of its particles changed considerably. This change was caused by the wear of the coating. Zr or ZrO₂ mean values of particles size $\pm$ SD after the friction tests changed the most significantly (Table 1 and Table 2). The shape of particles in Zr and Co-Cr-Mo coatings became rounded because the sharp inequalities abraded on traction.

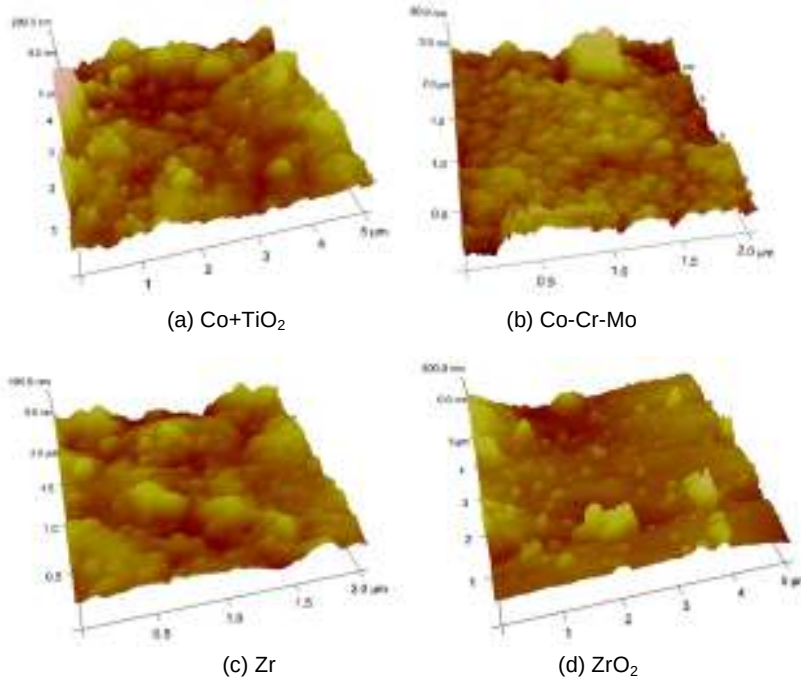


Figure 3. Coatings Co+TiO₂ (a), Co-Cr-Mo (b), Zr (c) and ZrO₂ (d) SPM-morphology images after the completed friction test. SPM surface morphology images after friction test for the coatings; (a) Co+TiO₂, (b) Co-Cr-Mo, (c) Zr, and (d) ZrO₂

The average sizes of particles after friction test are provided in Table 2.

Coatings			
Co+TiO ₂	Co-Cr-Mo	Zr	ZrO ₂
Mean values $\pm$ SDs			
139,6 $\pm$ 64,02	62,22 $\pm$ 28,56	74,9 $\pm$ 37,27	200,56 $\pm$ 46,01

Table 2. The average mean values of particles sizes (nm) after the completed friction test. Data are given in Mean±SD.

After comparing SPM surface morphology images of coatings prior to the friction tests and after them and the statistical evaluation, we can state that Co+TiO₂ coating has demonstrated the best durability and the highest abrasion resistance. The results of the test showed that the adhesion of the majority of coatings to polyethylene was insufficient and the coatings were worn out soon. This fact shows that prior to application of coating onto polyethylene its surface should be duly prepared and modified to change its hydrophilic and adhesive properties.

4. CONCLUSION

1. UHMWPE causes problems related to the operational life of components of the hip joint prosthesis.
2. The durability and the service life of coatings applied by magnetron sputtering are different for various combinations of metal and ceramic coatings. ~~The accomplished friction tests and statistical evaluations have showed that~~ UHMWPE with Co+TiO₂ coating have demonstrated the best durability and the highest abrasion resistance.
3. During the experiment, the vast majority of coatings have wore considerably. This circumstance may cause the formation of favorable conditions for accumulation of worn out granules around the implant. The application of the coatings of other materials onto polyethylene requires deeper investigation.

REFERENCES

1. Sundfeldt M., Carlsson L. V., Johansson C. B., Thomsen P. and Gretzer C. Aseptic loosening, not only a question of wear. A review of different theories. Acta Orthopaedica 2006; Taylor & Francis 2006. ISSN 1745–3674. Printed in Sweden. 77 (2): 177–197
2. Bombac, D., Brojan, M., Krkovič, M., Turk, R., Zalar, A. Characterization of titanium and stainless steel medical implants surfaces. Journal of Materials and Geoenvironment. 2007;54-2:151-164.
3. Bragolan, C. R., O'Coner, D. O., Lowenstein, J. D., Jasty, M., Biggs, S. A., Harris, W. H. A New Pin-on-Disk Wear Testing Method for Simulating Wear of Polyethylene on Cobalt-Chrome Alloy in Total Hip Arthroplasty. Journal of Arthroplasty. 2001;16-5: 658-665.
4. Stea S., Visentin M., Granchi D., Ciapetti G., Donati A. E., Zanotti C., Toni A. Cytokines and osteolysis around total hip prostheses. Cytokine, Vol. 12, No. 10 (October), 2000: pp 1575–1579
5. Kurtz S. M. UHMWPE Biomaterials Handbook, Second Edition: Ultra High Molecular Weight Polyethylene in Total Joint Replacement and Medical Devices. 2009, 568 psl.
6. Ratner D., Hoffman A. S., Schoen F. J. and Lemons J. E. Biomaterials science an introduction to materials in medicine. Elsevier, Academic Press, 2013, 1555 p.
7. Leeds, P., Dearnley, A. A review of metallic, ceramic and surface-treated metals used for bearing surfaces in human joint replacements, Proceedings/Institution of Mechanical Engineers. 2001; 213 (2):107-135.
8. Rahaman, M. N., Yao, A. Ceramic for Prosthetic Hip and Knee Joint Replacement. Journal of American Ceramic Society. 90 [7], 2007:1965-1988.

- 245 9. Rieker, C. B. Tribology in Total Hip Arthroplasty – Historical Development and
246 Future Trends. *Journal of Bussiness Briefing: Global Surgery*. 2003:1-3.
- 247 10. Tuller, M. B., Bellare, A. A study of the nanostructure and tensile properties of Ultra-
248 high molecular weight polyethylene. *Journal of Biomaterials*. 2004;25: 3389-3398.
- 249 11. Dumbleton, H. J., Manley, M. T., Edidin, A. A. A literature review of the association
250 between wear rate and osteolysis in total hip arthroplasty. *Journal of Arthroplasty*.
251 2002; 17,5: 649-661.
- 252 12. Desmet, T., Morent, R., Geyter, N. D., Leys, C., Schacht, E., Dubrue, P. Nonthermal
253 Plasma Technology as a Versatile Strategy for Polymeric Biomaterials Surface
254 Modification: A Review. *Biomacromolecules*. 2009; Vol. 10, 9:2351-2378
- 255 13. Shrojal, M. Desai, Singh, R. P. Surface Modification of Polyethylene. Long Term
256 Properties of Polyolefins. *Advances in Polymer Science*. 2004; Vol. 1, 69:231-294.
- 257 14. Mariūnas, M., Karavackaitė, J. Investigation of biological lubricants influence on the
258 durability of endoprostheses, *Lecture Notes of the ICB Seminars Biomechanics:*
259 *Customized Endoprosthesis – Design, manufacture and Clinical Application*. Warsaw,
260 2003:-59-63.
- 261 15. Mariūnas, M., Šešok, A., Lisauskas, V. Investigation of Possibilities for Ceramic
262 Coating of Biological Polyethylene Implants. *Solid State Phenomena*. 2006;Vol. 113:
263 549-555.
- 264 16. Joon Park. P.S.Lakes. *Biomaterials. An Introduction*. Third Edition, Springer, USA,
265 2007, 535 p.