

EXPERIMENTAL RESEARCH OF THE DURABILITY OF UHMWPE IMPLANTS WITH DIFFERENT COATING STRUCTURE AND DURABILITY

Formatted: Centered

Comment [L1]: COATINGS

Formatted: Font: 18 pt

Comment [L2]: Title shall be more specific for the method and the materials that author have used.

ABSTRACT

The article examines structure of implants coatings using scanning probe microscope. Osteolysis, artificial hip joint components, materials, UHMWPE coatings other coatings and magnetron sputtering method, which is used to coat UHMWPE, are discussed. The experimental Co+TiO₂, Co-Cr-Mo, Zr and ZrO₂ coatings microstructure research before and after the friction test have been done. During research, 15 % polyvinylpyrrolidone has been used 15 % polyvinylpyrrolidone as a an artificial joint lubricant, and the friction test has been carried out in vertical plane and UHMWPE samples wereas rubbed at the same working conditions. It has been determinated that after the friction test Co+TiO₂ coating has shown the best endurance and greatest abrasion resistance. However, this coating also wore considerably after 10 000 cycles. This circumstance may cause formation of favorable conditions for accumulation of worn out granules around the implant. 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.

Comment [L3]: Coatings and the methods should be mentioned in two different sentences.

Formatted: 20 - Reziime tekstas, Right: 0.24"

Keywords: implants, coating, scanning probe microscope, durability

1. INTRODUCTION

Development of replacement arthroplasty touched a number of problems. They include a design of the implanted component, a way of its fixation, its properties, rubbing surfaces and their wear resistance. (ref?) In scientific publications of the last decade, the consequences of wear of articular surfaces, such as osteolysis and survival of mechanical fixing components, are frequently discussed upon. (ref?) Osteolysis is understood as bone resorption or massive formation of cystic granuloma around the an implant or massive formation of cystic granuloma. (ref?) The bone resorption around the implanted hip joint components is one of topicalities of today surgical replacement arthroplasty that predetermines the service life of the mechanical fixtures of the implanted component. (ref?)

Comment [L4]: What are «they»?

Comment [L5]: «They» becomes «it»? Subject here is singular or plural??

Comment [L6]: Same as L4.

Comment [L7]: Same as L4

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 and so on) [1, 2, 3], ceramics (aluminum oxide, zirconium oxide-zirconia and so on) [4] and polymeric materials (PMMA, UHMWPE) [5, 6]. Polymeric materials usable-used in the production of the implants are-have become abundant; however, for over 40 years, Ultra-High Molecular Weight Polyethylene (UHMWPE) is used in the production of hip joint endoprotheses. (ref?) The said material is used for producing an-the insert of the hip joint socket. (ref?) It is distinguished for its low friction coefficient, good biocompatibility and lubricant properties; however, its break

resistance is lower, ~~so it wears rapidly leading it to rapid wear.~~(ref?) In addition, particles of worn polyethylene get into the body and cause undesirable reaction of tissues, known as osteolysis [7]. In such a case, the patient ~~is becomes~~ a subject ~~to for a~~ revision surgery of the hip joint replacement arthroplasty.

At present, the modification of metal or plastic surfaces of the implants is very often explored [8, 9]. The modification of a polymer surface, either by chemical or physical methods, is very important in order to achieve new uses and different properties. This is especially true when referred to inert polymers, as is the case of polyethylene, whose surface needs etching treatments to improve ~~its their biocompatibility and their~~ adhesion ~~with via~~ printing or decoration finishes and ~~also its biocompatibility~~ [4-6].

The previous researches [10] have shown that when the elasticity module of the material of hip endoprosthesis socket is small and the stiffness of femoral stem is big, the pressure in contact surfaces is reduced considerably, lubrication conditions are improved and the durability of hip endoprosthesis is increased. The researches [11] have shown that when coating the polyethylene surface of the socket with durable ~~TiO₂ and Co-Cr-Mo~~ coatings, ~~TiO₂ and Co-Cr-Mo~~ on one side the ~~contact surfacesurface contact~~ is hardened but on the other side it is coated on a resilient base and ~~this~~ allows it to increase the ~~contact surfacesurface contact~~. Such solution helps to reduce stresses and to 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, to undertakeing~~ damping of vibrations and impacts.

UHMWPE is coated 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 [11]. 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 pass ~~are subjected to~~ considerably higher number of cycles; in addition, ~~using of various coatings is possible~~. At present, zirconium and ~~zirconia zirconium oxide~~ are increasingly ~~often~~ used in ~~the~~ replacement arthroplasty. (ref??) Zirconium is distinguished for ~~its~~ good biocompatibility ~~properties~~ and its modulus of elasticity is close to ~~the~~ modulus of elasticity of human bones. (ref??)

In the present research, ~~we plan to apply~~ coatings of UHMWPE with ~~other materials (such as zirconium, zirconium oxide 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) ~~after application of the coatings before~~ and after the friction tests ~~and~~ to identify what coating withstood 10 000 working cycles in the best way.

2. MATERIALS AND METHODS

For ~~the~~ formation of the coatings, 3-source magnetron sputtering SCM was used.

~~the~~ magnetron sputtering method was chosen. ~~The method was chosen because since the~~ application of coatings takes place at 70°C, ~~so the 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 by: oxide coatings can be sputtered (reactive sputtering), excellent layer uniformity, very smooth sputtered coatings (no droplets). Magnetron sputtering technology has some disadvantages: slow deposition speed and adhesion of coatings is lower and density of the sputtered layers may be lower. 3-source magnetron sputtering SCM was used.~~

Comment [L9]: Meannless. Shall find an appropriate term to say this.

Comment [L10]: Of what?

Comment [L11]: Shall be at the enf of the sentence.

Comment [L12]: Either «elastic module» or «modulus of elasticity» shall be used. Please CTRL+F the whole text for that term and correct them.

Comment [L13]: Low?

Comment [L14]: High?

Comment [L15]: Same as L10.

Comment [L16]: What is «it»?

Comment [L17]: ???

Comment [L18]: This paragraph belongs to either Introduction od Discussion and shall be modified accrodingly. So it shall be removed to one of these sections. Here the authors shall briefly give the experimental conditions for magnetron sputtering.

In course of the works [11], on the base of the carried out tests and their results, we selected the coating that showed them the best on the primary tests: Co-Cr-Mo, Co+TiO₂; in addition, we used Zr and ZrO₂ coatings, because they increasingly often are applied in production of implants.

In the works, special UHMWPE usable for medical applications (*Chirulen* (ISO5834-2, from *POLY Hi Solidur MediTECH* company) was used. UHMWPE was coated with Co+TiO₂, Co-Cr-Mo, Zr and ZrO₂. The thickness of the said coatings is 2 µm.

The surface of samples has been measured by scanning probe microscope (SPM) (Dimension 3100, produced by company Digital Instruments, Country??). In comparison with profilometer, microscope is characteristic of much larger resolution in respect of X and Y axes (0,1-3 nm) and Z axis (0,01 nm). Measures have been taken by microscope set for tapping mode. This mode is applied when larger horizontal resolution is necessary. The needle of the microscope vibrates at frequency close to resonance and touches the surface of the sample periodically. The amplitude of needle vibration comes up to 20-100 nm. Information on the surface of the sample is obtained upon combination of data related to the movement of a piezo scanner at the direction of Z axis and the change in probe vibration phase.

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

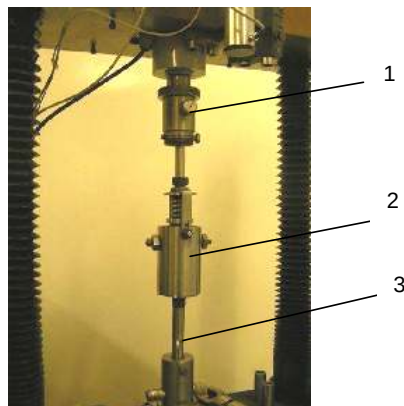


Figure 1. Stand of the experiment: 1– FP-10 tensioning equipment; 2 – special device; 3 – rod

The device for the stand is intended for operation in the German-made FP-10 tensioning equipment (Company, Country??). 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 a 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 (what angle?). 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.

After the wearing tests, the microstructure of the coatings was examined again by a scanning probe microscope. Finally, an analysis of the obtained results was carried out.

Comment [L19]: Belongs to discussion while explaining while you chose these coatings.how many specimens were used for coating? How many specimen numbers were prepared for each group? What is n=?

Comment [L20]: Authos should give details for the experimental coating conditions briefly.

Comment [L21]: Same as L18.

Comment [L22]: Same as L18

Comment [L23]: Measured for what?

Comment [L24]: Belongs to discussion. Authors should give details for experimental conditions for SPM. What is the scanning distance/area?...

Comment [L25]: How many cycles? For how long? How many specimens used? What are the experimental conditions? Eg:temperature, wet, dry?? How many times the tests were repeated? What is the statistic method?

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 course of analysis of the photos of the surface of coatings made by a scanning probe microscope (Fig. 2), it was found that the largest agglomerates of granules are formed in Co-Cr-Mo coating (about 2 μm long, 7 μm wide and 10 nm high). The roughness of Zr coating is the minimum; however, it includes large agglomerates of granules (1.5×1.7 μm). Zirconium is known as a crystal structure comminuting agent and shows particularly good granular structure refinement effect. The roughness of ZrO₂ coating is relatively low (3.2×2.5 μm); however, the structure of the coating consists of large granules. Co+TiO₂ coating is of a moderate roughness with 4.5×4.5 μm granular agglomerates.

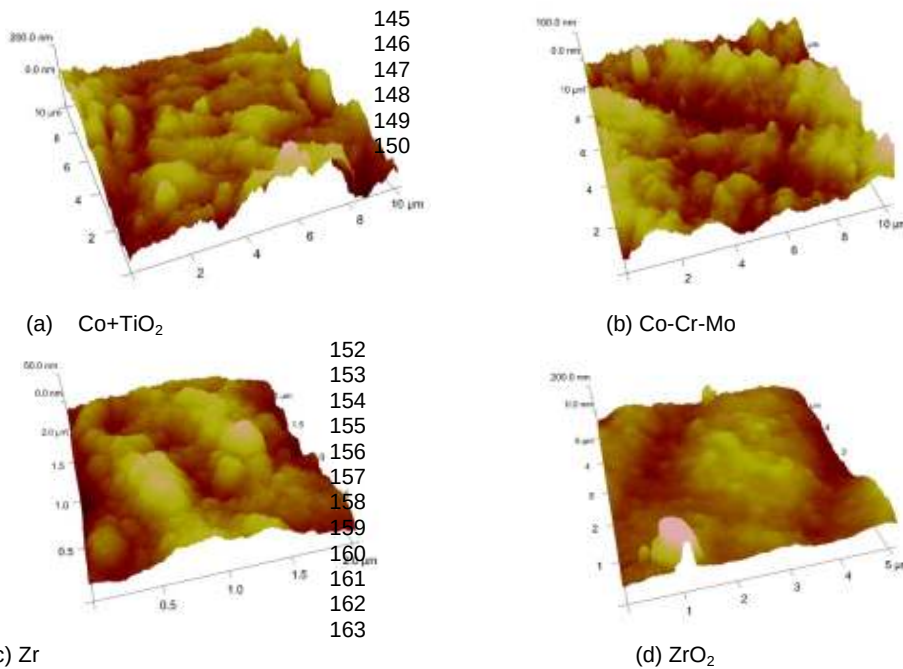


Figure 2. SPM surface morphology images before friction test for the coatings; (a) Co+TiO₂, (b) Co-Cr-Mo, (c) Zr, and (d) ZrO₂.

It was found that after application of coating with Co+TiO₂ coating by magnetron sputtering the sizes of granules are from were found to be between 50 nm to and 200 nm, so the surface is creating a rough surface enough. The sizes of granules in Co-Cr-Mo coating vary between 20 nm and 100 nm; the granules are oval with striking sharp inequalities. The sizes of granules in Zr coating vary between 8 nm and 50 nm; it is a surface of the minimum grain

Formatted: Left

Formatted: Subscript

Comment [L26]: There is no other technique already.

Comment [L27]: There are no «granules» here. Granules are whole spherical structures. Here you have rough surface profiles with round hills and valleys. This is the physical appearance of the surfaces. But, they are different in terms of their surface roughnesses. And you have start to discuss over at Table 1 at this point.

and roughness. The sizes of granules in ZrO₂ coating vary between 85 nm and 200 nm, and the surface is rough enough.

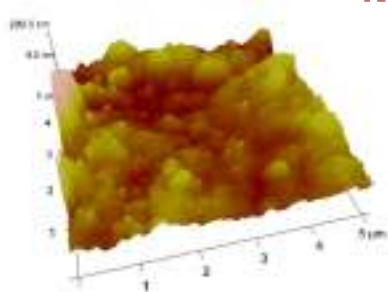
The average sizes of granules are provided in Table 1-below.

Table 1. The values of average sizes of granules, nm

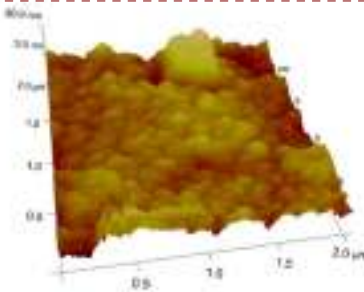
Coating							
Co+TiO ₂		Co-Cr-Mo		Zr		ZrO ₂	
Sizes of granules, nm							
min	max	min	max	min	max	min	max
50+2.5	200+5.2	20+1.8	100+4.2	8+1.2	50+3.2	85+3.5	200+6.4

Table 1. The average values of granule sizes (nm).

On durability and wearing tests, 10 000 cycles were applied upon the load of 400 N. On the analysis of the photos of Co+TiO₂, Co-Cr-Mo, Zr and ZrO₂, coatings made by a scanning probe microscope (SPM) after the tests on friction stand, it was found that Co+TiO₂ coating was distinguished for the best mechanical properties, because the changes of its grain and the shape of its granules were inconsiderable. ZrO₂ showed the worst mechanical properties: it may 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 granules changes considerably. This change was caused by wear of the coating. The surface of Co-Cr-Mo coating wore by 20 %. The shape of granules in Zr and Co-Cr-Mo coatings became rounded, because the sharp inequalities abraded on traction. Thus, the roughness of the surface was reduced.



(a) Co+TiO₂



(b) Co-Cr-Mo

Comment [L28]: At the tables you have the average min and max values. You should be giving mean values ± SDs. And you have to discuss over these mean values to compare the roughness of the coatings. You should also tell if there are/are not any statistical difference between the coatings. We need p values. And you shall be explaining why these surfaces are similar or different. Add a paragraph regarding that.

Formatted: Left

Comment [L29]: Belongs to material and methods.

Comment [L30]: No granules!!

Comment [L31]: How do you suggest that? Have you made a statistical evaluation for before and after? What are the p values?

Comment [L32]: You can only support your quantified results with these quality experiments like images. Seeing is not enough, you have to support with numerical values and statistics.

Comment [L33]: How did you measure and conclude that??

Comment [L34]: The whole paragraph is written with lack of scientific evidence...Please support with statistical evaluation!

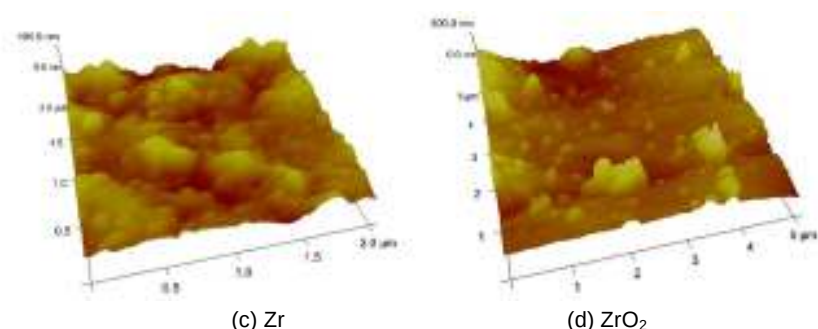


Figure 3. Coatings Co+TiO₂ (a), Co-Cr-Mo (b), Zr (c) and ZrO₂ (d) SPM morphology images after completed friction test

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

Table 2. The values of average sizes of granules after completed friction test, nm

Coating							
Co+TiO ₂		Co-Cr-Mo		Zr		ZrO ₂	
Sizes of granules, nm							
min	max	min	max	min	max	min	max
50±3.0	200±5.8	20±2.4	80±5.6	20±2.2	100±2.5	140±4.5	250±7.2

So, after comparing the morphological photos of the structure of coatings made by a scanning probe microscope prior to the friction tests and after them, we can state that Co+TiO₂ coating had demonstrated the best durability and the highest abrasion resistance; however, this coating wore considerably. The last circumstance may cause formation of favorable conditions for accumulation of worn out granules around the implant. The results of the test showed that adhesion of a majority of coatings to polyethylene is 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. Taking into account the results of the carried out analysis of the materials usable for hip joint replacement arthroplasty, we can conclude that using UHMWPE causes problems related to 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. It was found that the coatings obtained were nanocrystalline.
2. After the analysis of the morphological photos of the structure of coatings made by a scanning probe microscope prior to the friction tests and after them, we can state that Co+TiO₂ coating had demonstrated the best durability and the highest abrasion resistance.
3. However, this coating also wore considerably after 10 000 cycles. Eksperimento metu danges nemažai nusitino. During the experiment, the vast majority of coatings wore considerably. This circumstance may cause formation of favorable conditions for accumulation of worn out granules around the implant. This fact shows that prior to

Comment [L35]: Modify like L27.

Formatted: Font: Arial

Comment [L36]: Scientific manuscript don not start with so, because.....

Comment [L37]: These are «SPM surface morphology images». You shall always use the same technical term throughout the manuscript.

Comment [L38]: You can't state since you don't give statistical values!!!

Comment [L39]: You have used «steadfastness» before! Which one??

Comment [L40]: Discussion has no references. You didn't compare your study with any other studies. You supply ref only 11 ref for the Introduction section (which wasn't enough). You should discuss your outdrawings with the other studies.

Comment [L41]: If you decide to give bulleted conclusions you need to be specific and brief.

Comment [L42]: This is not a conclusion to be drawn.

Comment [L43]: Steadfastness??

Comment [L44]: Were considerably what?

application of coating onto polyethylene, its surface should be duly prepared and modified to change its hydrophilic and adhesive properties. So, application of coatings of other materials onto polyethylene requires deeper investigation.

REFERENCES

1. Bombac, D., Brojan, M., Krkovič, M., Turk, R., A. Zalar, A. Characterization of titanium and stainless steel medical implants surfaces. *Journal of Materials and Geoenvironment*. 2007;54-2:151-164.
2. 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.
3. 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 (H): 107-135.
4. Rahaman, M. N., Yao, A. Ceramic for Prosthetic Hip and Knee Joint Replacement. *Journal of American Ceramic Society*. 90[7], 2007:1965-1988.
5. Rieker, C. B. Tribology in Total Hip Arthroplasty – Historical Development and Future Trends. *Journal of Bussiness Briefing: Global Surgery*. 2003:1-3.
6. Tuller, M. B., Bellare, A. A study of the nanostructure and tensile properties of Ultra-high molecular weight polyethylene. *Journal of Biomaterials*. 2004;25: 3389-3398.
7. Dumbleton, H. J., Manley, M. T., Edidin, A. A. A literature review of the association between wear rate and osteolysis in total hip arthroplasty. *Journal of Arthroplasty*. 2002;17, -5: 649-661.
8. Desmet, T., Morent, R., Geyter, N. D., Leys, C., Schacht, E., Dubruel, P. Nonthermal Plasma Technology as a Versatile Strategy for Polymeric Biomaterials Surface Modification: A Review. *Biomacromolecules*. 2009; Vol. 10, 9:2351-2378
9. Shrojal, M. Desai, Singh, R. P. Surface Modification of Polyethylene. Long Term Properties of Polyolefins. *Advances in Polymer Science*. 2004; Volume 169:231-294.
10. Mariūnas, M., Karavackaitė, J. Investigation of biological lubricants influence on the durability of endoprostheses, *Lecture Notes of the ICB Seminars Biomechanics: Customized Endprosthese – Design, manufacture and Clinical Application*. Warsaw, 2003; -59-63.
11. Mariūnas, M., Šešok, A., Lisauskas, V. Investigation of Possibilities for Ceramic Coating of Biological Polyethylene Implants. *Solid State Phenomena*. 2006; Vol. 113:549-555.

Comment [L45]: You can't conclude that. Since you haven't shown the worn out granules present around the implant with SEM micrographs. You also didn't do any hydrophilicity or adhesive property experiments so you can't mention these.

Comment [L46]: References are between 2001-2009. You need to find up to date references. What about 2012-2015??

Comment [L47]: No referece for discussion??

Comment [L48]: ???

Comment [L49]: ???

Comment [L50]: ??

Comment [L51]: ???

Comment [L52]: ??

Comment [L53]: ???

Comment [L54]: ????

Comment [L55]: ???

Comment [L56]: ????????????