# Corrosion degradation of spacers – examination of changes in bone cement coating

# Degradacja korozyjna spacerów – badanie zmian w powłoce z cementu kostnego

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STRESZCZENIE

Spacer jest specjalnym implantem stosowanym w momencie wystąpienia infekcji po zabiegu endoprotezoplastyki. W organizmie człowieka spacery są narażone na procesy degradacyjne. W tym artykule przyjrzano się wpływowi korozji na spacery. Poddano badaniom korozji elektrochemicznej piny tytanowe z powłoką z cementu kostnego w dwóch roztworach: roztworze Ringera i sztucznej ślinie. Do badań wykorzystano cement kostny o niskiej i wysokiej lepkości. Wyznaczono gęstość prądu korozyjnej oraz potencjał korozyjny dla próbek tytanowych i próbek tytanowych z powłoką z cementu kostnego oraz wyznaczono potencjodynamiczną krzywą polaryzacji dla najoptymalniejszej powłoki. Topografia próbek była analizowana przy wykorzystaniu mikroskopii SEM. Przyjrzano się zmianom jakie zaszły na powłoce w wyniku działania procesów degradacyjnych wywolanych korozją elektrochemiczną. Stwierdzono, że powłoka z cementu kostnego o wysokiej lepkości polepsza odporność korozyjną spacerów, jednakże w efekcie dochodzi do jej nieodwracalnych zmian, tj. wytrawienie na całej powierzchni, powstanie porów czy kraterów oraz miejscowe intensywne zniszczenia powłoki. Zakłada się, że należy kontynuować badania degradacji korozyjnej dla spacerów i cementu kostnego, gdyż w literaturze światowej brakuje tego typu pozycji.

ABSTRACT

Spacer is a special implant used at the time of infection after endoprosthetic surgery. It consists of a metal core and bone cement coating with an antibiotic. In the human body spacers are exposed to degradation processes. This paper looks at the effect of corrosion on spacers. Electrochemical corrosion tests were performer on titanium pins with bone cement coating in two solutions: Ringer's solution and artificial saliva. Bone cement with low and high viscosity was used. Corrosion current density and corrosion potential for titanium specimens and titanium specimens with bone cement coating were determined. Additionally, the potentiodynamic polarization curves for the most optimal coating was determined. The topography of the specimens were analyzed using SEM microscopy. Changes on the coating due to electrochemical corrosion were observed. It has been found that high viscosity bone cement improves corrosion resistance of spacers, however, resulting in irreversible changes, i.e. etching the whole surface, pores and craters formation and local intense coating damage. It is assumed that corrosion degradation tests for spacers and bone cement should be continued, as this type of item is missing in the world literature.

***Słowa kluczowe:*** *spacery, implanty tytanowe, cement kostny, degradacja korozyjna, niszczenie implantów.*
***Key words****: spacers, titanium implants, bone cement, corrosion degradation, implant devastation.*

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## INTRODUCTION

Spacer is a special type of endoprosthesis applied at the time of infection after endoprosthetics surgery. This implant consist of a metal core covered with bone cement, which contains an antibiotic. Spacers are used for local therapy and for treating an infected site. After the treatment of the joint, a typical endoprosthesis is used [1-3].

Implanted into the body, the spacers are exposed to various types of degradation processes. One of them is corrosion, i.e. spontaneous destruction caused by chemical reactions, electrochemical, microbiological or physical processes. The human body is a very aggressive environment, this is due to: a corrosive chemical composition, acidic pH and relatively high temperature [4-7].

In the world literature it is hard to find research on the degradation of spacers in an aggressive human environment. The most popular test concerning bone cement is the retention of samples in SBF solution and 37 degrees [8-10], but this type of study only analyzes chemical degradation and does not include electrochemical corrosion.

In this work, the impact of accelerated corrosion degradation on spacer, in particular the bone cement coating will be investigated.

## MATERIAL AND METHODS

Corrosion studies were performed on two types of specimens: titanium specimens (6x) and titanium specimens with bone cement coating (12x) immersed in simulated body fluid solutions (SBF). The specimens before the study were: ground, skimmed and covered with an insulating resin. The area affected by corrosion was 10x10 mm (Fig. 1). For the study was used low and high viscosity bone cement - Cemex from Tecres Company.

*Fig. 1. Specimens immersed in artificial saliva*

Studies were performed in 2 types of SBF solutions at room temperature according to the guidelines PN-EN ISO 10993-15 [11]. The SBF solutions were: Ringer solution /Tab. 1/ and Artificial Saliva prepared by dissolving of the reagents according to Tab. 2. [12].

Tab. 1. Composition of Ringer solution at pH 5-7,5

| Reagents | Quantity $g \cdot L^{-1}$ |
|---|---|
| NaCl | 8.6 |
| KCl | 0.3 |
| $CaCl_2 \cdot 2H_2O$ | 0.33 |
| NaOH | to set pH |
| HCl | to set pH |

Tab. 2. Composition of artificial saliva at pH 8.3 [2]

| Reagents | Quantity $g \cdot L^{-1}$ |
|---|---|
| $(NH_2)_2CO$ | 0.13 |
| NaCl | 0.7 |
| $NaHCO_3$ | 1.5 |
| $Na_2HPO_4$ | 0.26 |
| $K_2HPO_4$ | 0.2 |
| KSCN | 0.33 |
| KCl | 1.2 |

Three electrodes were used in the study: counter electrode (standard platinum electrode), reference electrode (Ag/AgCl saturated with potassium chloride KCl) and electrode discharged from the test sample. In the studies corrosion potential (Ecorr) and corrosion current density (Icorr) were specified from the polarization curves by using the Tafel extrapolation method (Fig. 2). Example application of this method is shown on Fig. 3.

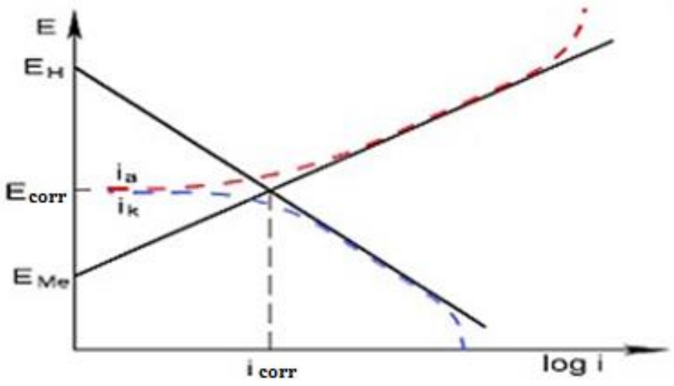



Fig. 2. Scheme of Tafel extrapolation (red line – extrapolation of the cathode branch, blue line – extrapolation of the anode branch)

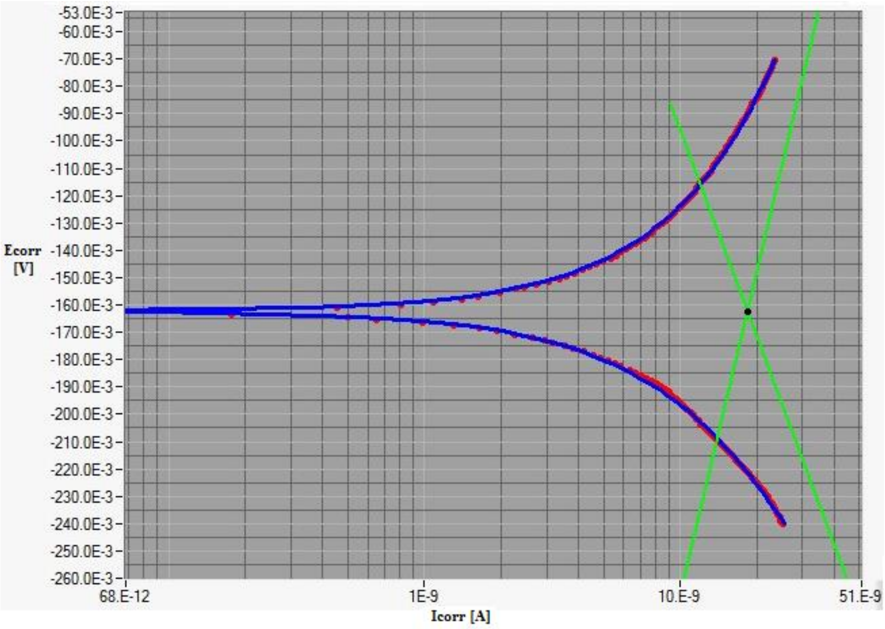



Fig. 3. Sample Tafel extrapolation chart for titanium specimen with bone cement coating (Ringer’s solution, high viscosity bone cement)

The studies were conducted on potentiostat/galvanostat Atlas 0531 (Atlas Solich). The parameters were as follows: a potential change rate - 1 mV/s, a scan range 600-2000 mV. The test stand is shown in Fig. 3.


*Fig. 3. Corrosion test stand*

## RESULTS AND DISCUSSION

For the titanium specimens immersed in Ringer’s solution the following average results were obtained: corrosion current density Icorr = 51.04 nA/cm$^2$ and corrosion potential Ecorr = -373.33 mV. Whereas for the titanium specimens with bone cement coating averange Icorr = 50.02 nA/cm$^2$ and Ecorr = -354.12 mV for low viscosity bone cement and Icorr = 14.74 nA/cm$^2$ and Ecorr = -477.73 mV for high viscosity bone cement. Detailed results are shown in Tab. 3. Sample potentiodynamic polarization curves for one titanium specimen and one titanium specimen with bone cement coating is shown on Fig. 4.

For the titanium specimens immersed in Artifical Saliva solution the following average results were obtained: corrosion current density Icorr = 25.72 nA/cm$^2$ and corrosion potential Ecorr = -404.24 mV. Whereas for the titanium specimens with bone cement coating averange Icorr = 17.72 nA/cm$^2$ and Ecorr = -340.49 mV for low viscosity bone cement and Icorr = 6.42 nA/cm$^2$ and Ecorr = -413.83 mV for high viscosity bone cement. Detailed results are shown in Tab. 3.

Tab. 3. Corrosion test results

| Solution: | Ringer's | | | Artificial Saliva | | |
|---|---|---|---|---|---|---|
| Specimens: | Titanium | Titanium with bone cement coating | | Titanium | Titanium with bone cement coating | |
| | | Low viscosity | High viscosity | | Low viscosity | High viscosity |
| Icorr [nA/cm$^2$] | 53.26 | 54.92 | 18.31 | 26.24 | 23.52 | 6.75 |
| | 64.45 | 43.63 | 16.23 | 21.37 | 18.23 | 4.23 |
| | 35.42 | 51.53 | 9.67 | 29.54 | 11.43 | 8.27 |
| Ecorr [mV] | -392.91 | -354.43 | -463.32 | -386.94 | -339.82 | -429.58 |
| | -372.24 | -371.68 | -494.23 | -407.35 | -357.43 | -398.29 |
| | -354.85 | -336.25 | -475.64 | -418.44 | -324.24 | -413.62 |

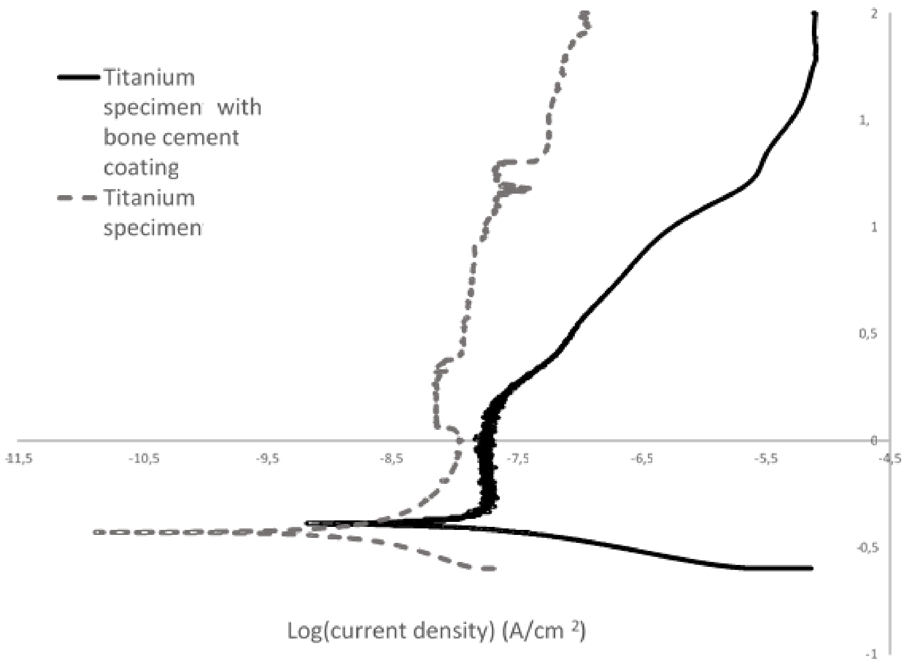



*Fig. 4. Sample potentiodynamic polarization curves of tested specimens in Ringer solution (spacer based on high viscosity bone cement)*

It can be stated that the high viscosity bone cement coating reduces the corrosion current density by an average of 28.87% in Ringer's solution and 24.96% in Artificial Saliva solution and increase corrosion potential by 27.96% in Ringer's solution and 2.37% in Artificial Saliva solution. Fig. 4 shows the potentiodynamic polarization curves shift to the right, which means improved corrosion resistance.

Corrosion studies, however, affect to the structure of investigated materials. After the tests specimens were investigated using SEM microscopy. The topography of the titanium surface prior to the test is shown in Fig. 5 and of the bone cement surface in Fig 6. In contrast, Fig. 7, Fig. 8 and Fig. 9 show the topography after a corrosion test in SBF solution.

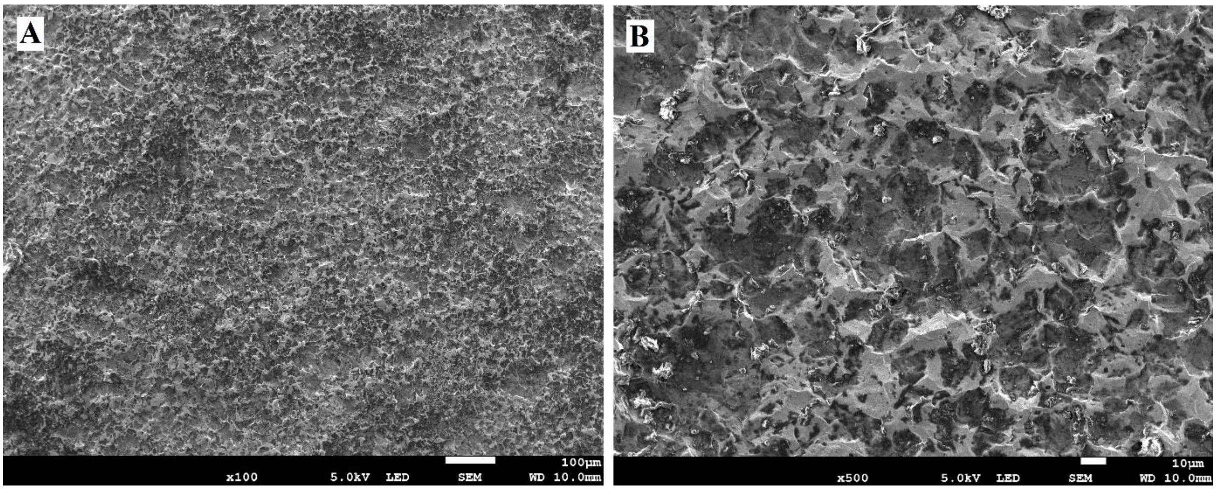



*Fig. 5. Topography of the surface of titanium before the corrosion test (A-100x, B-500x)*

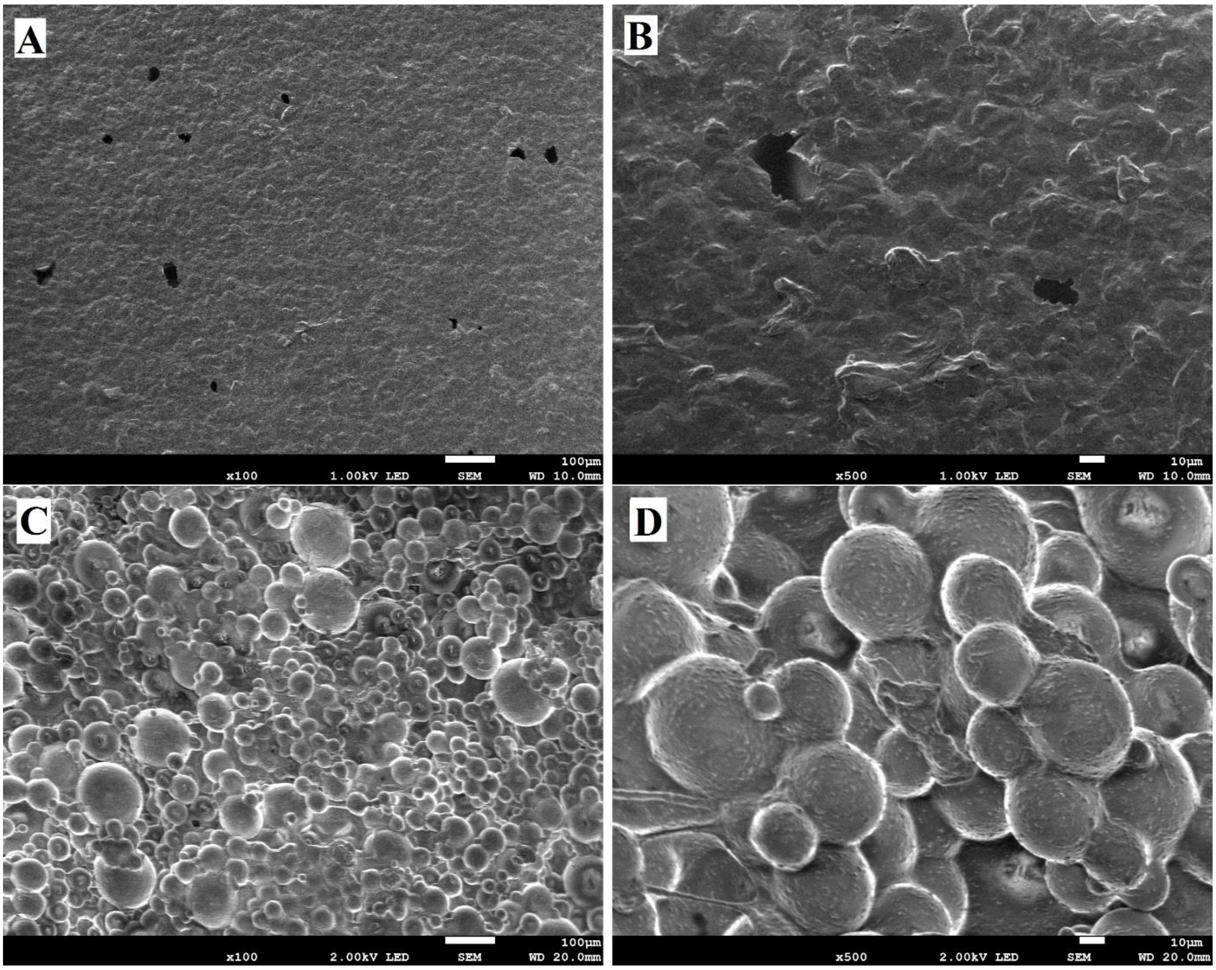



*Fig. 6. Topography of the surface of bone cement before the corrosion test (high viscosity: 100x –A and 500x – B, low viscosity: 100x – C and 500x – D)*

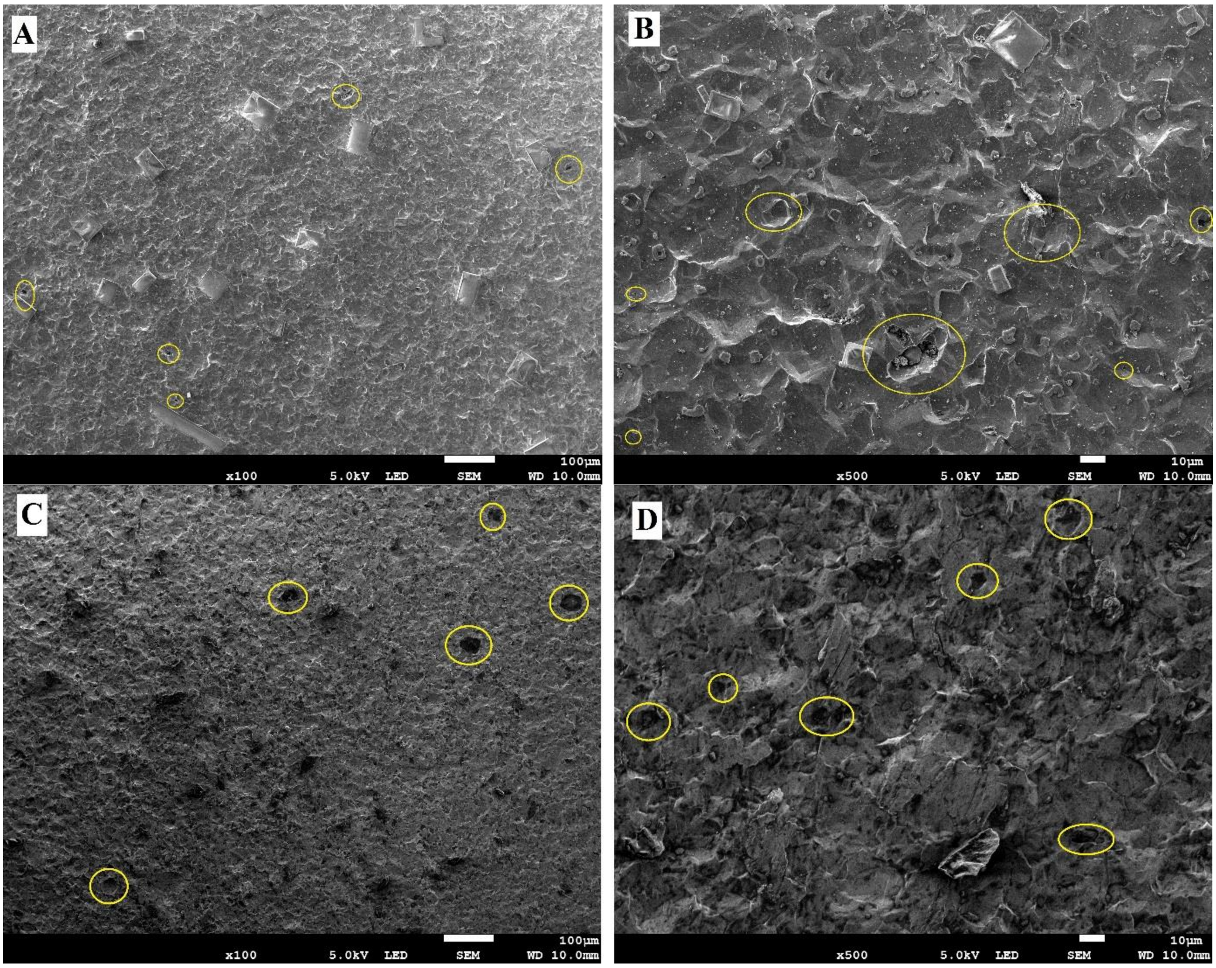
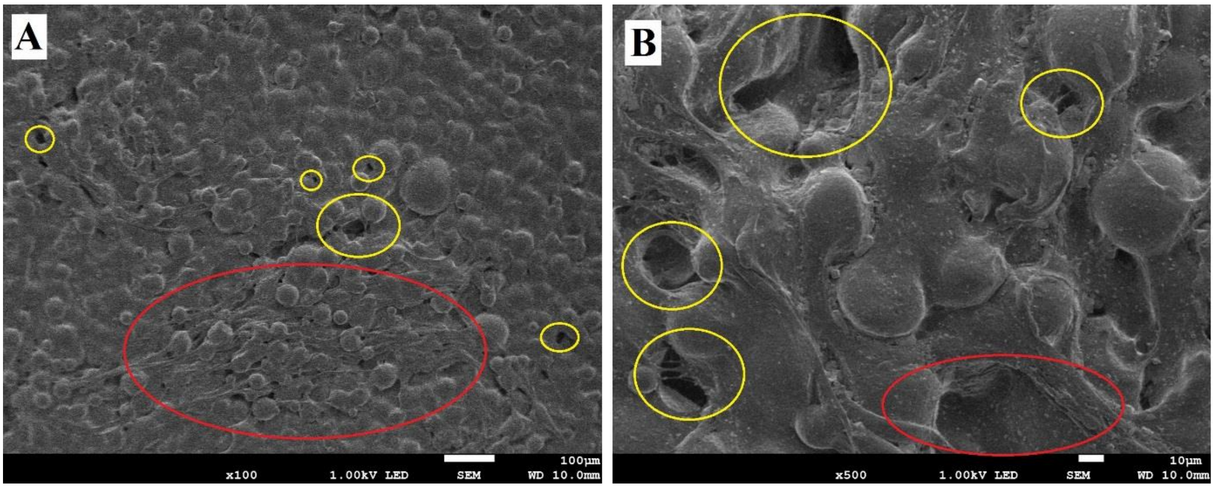



*Fig. 7. Topography of the surface of titanium after the corrosion test (Ringer's solution: 100x – A and 500x – B, Artificial Saliva solution: 100x – C and 500x – D, yellow circles – micropores/craters)*



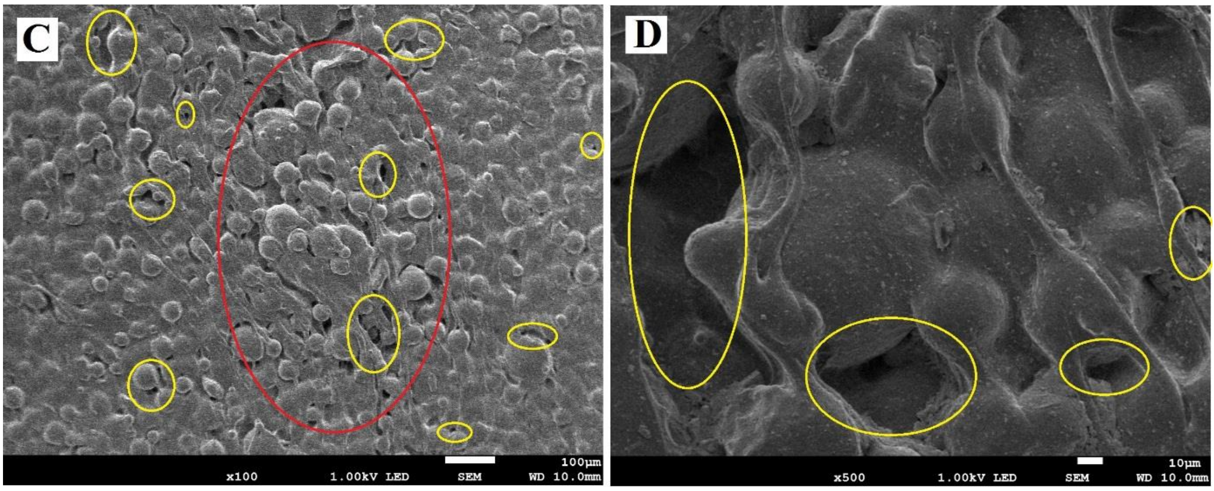


*Fig. 8. Topography of the surface of high viscosity bone cement after the corrosion test (Ringer's solution: 100x – A and 500x –B, Artificial Saliva solution: 100x – C and 500x –D, yellow circles – micropores/craters and red circles – areas of intense corrosion degradation)*

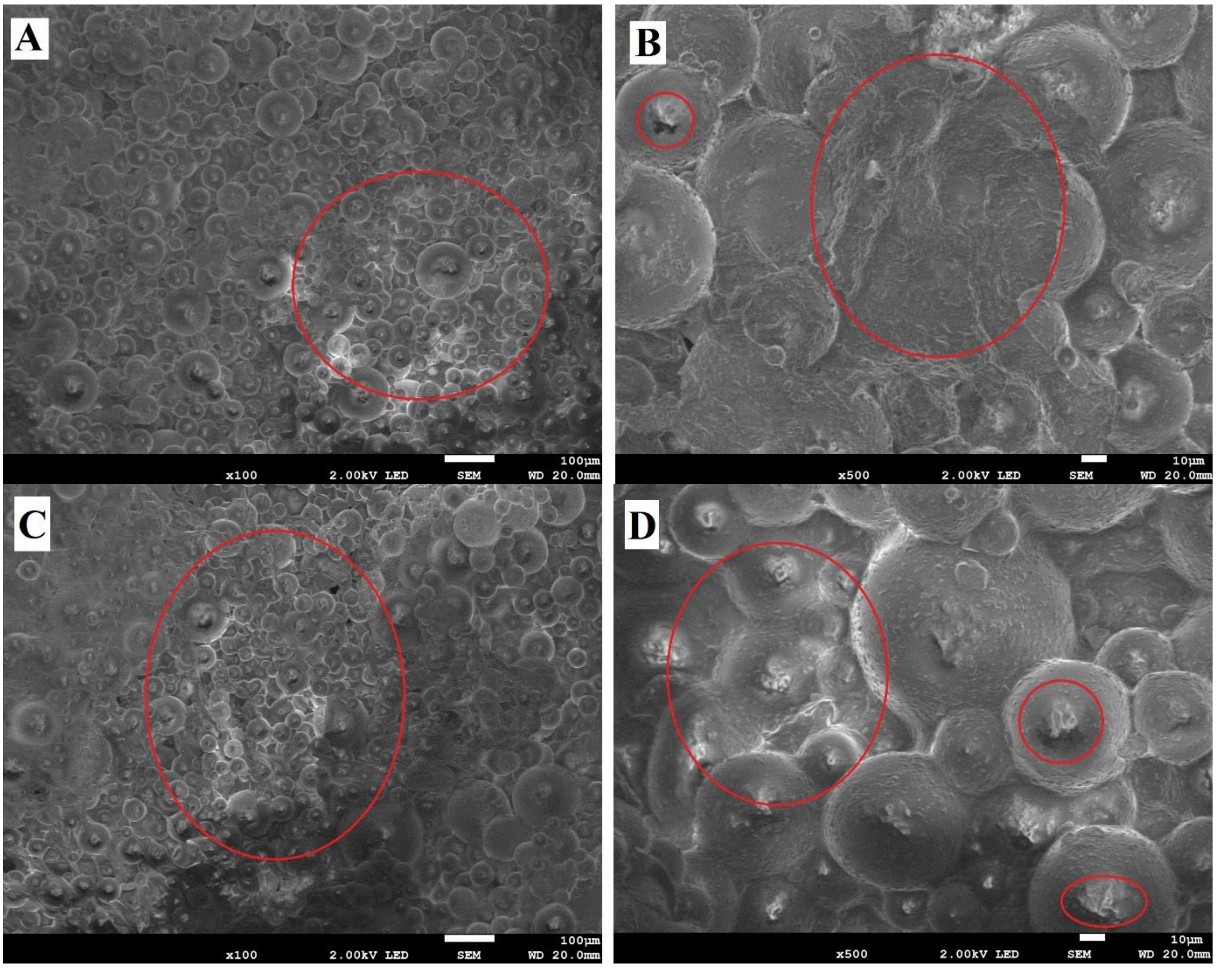


*Fig. 9. Topography of the surface of low viscosity bone cement after the corrosion test (Ringer's solution: 100x – A and 500x – B, Artificial Saliva solution: 100x – C and 500x – D, red circles – areas of intense corrosion degradation)*

As a result of corrosion tests on the outer surface of material it can be notice a significant change in its structure (circles in Fig. 7-9). In the case of titanium, melt areas and numerous micropores or craters (Fig.10) were observed and on bone cement general surface etching and areas of intense corrosion degradation were observed (Fig 11). It is suspected that the structure was dissolved/melted by the aggressive environment and corrosive currents.

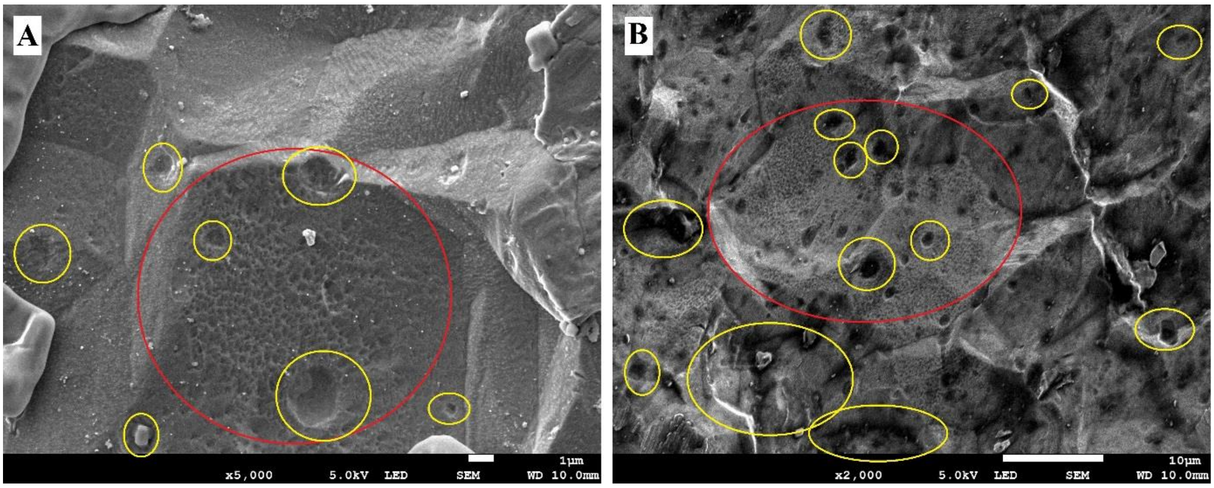



*Fig. 10. Corrosion changes on the surface of titanium specimens (Ringer's solution: 5000x – A, Artificial Saliva solution: 2000x – B, yellow circles – micropores / craters and red circles – areas of intense corrosion degradation)*

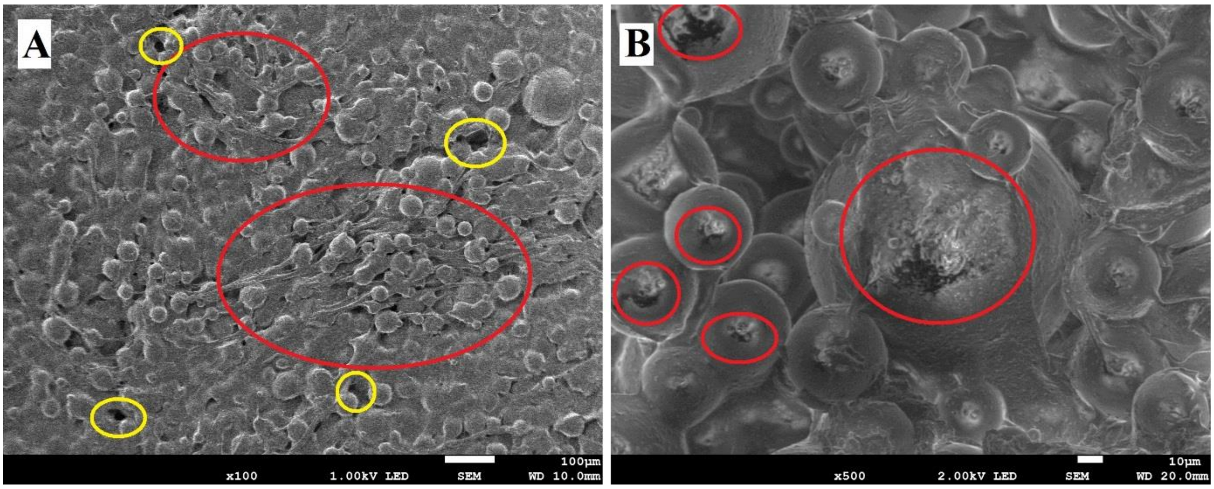



*Fig. 11. Corrosion changes on the surface of bone cement coating (Ringer's solution and high viscosity bone cement: 100x – A, Artificial Saliva solution and low viscosity bone cement: 500x – B, yellow circles – micropores / craters and red circles – areas of intense corrosion degradation)*

## CONCLUSIONS

- Spacers are guarded for corrosive degradation. In the research, both titanium and bone cement devastation occurred.
- Greater corrosion susceptibility was observed in Ringer's solution than artificial saliva, hence the choice of SBF solution is important for research.
- Low viscosity bone cement is not suitable for coating of spacers, because of their susceptibility to corrosive degradation and too porous structure. On the other hand, this type of coating can be expected to better fulfill the function, i.e. release of antibiotic particles.
- High viscosity bone cement improves the corrosion resistance (the corrosion current density decreased by an average of 26,92% and increase the corrosion potential by an average

15,17%), thence, it is assumed that they are more suitable for coating for spacers in terms of resistance to destruction in the human body.

- The effect of corrosion degradation on spacers are: etching of the outer surface, formation of pores or craters, occurrence of areas of intense degradation and even local shattering of the coating.
- It is assumed that further consideration is required for the effect of corrosion degradation on spacer and bone cement, particularly in terms of its biomechanical properties.

## REFERENCES


[1] M.Sukeik, F.S. Haddad: Two-stage procedure in the treatment of late chronic hip infections - spacer implantation. Int J Med Sci., 2009; 6(5): 253-257.

[2] http://tecres.pl/site/Spacer-polacco_nov08_indd.pdf.

[3] B. Weiss, S. Vanrell, M. Berli, S. Ubal, J. Di Paolo : Spacers in the treatment of hip joint infections: numerical analysis of their durability. Journal of Physics, 2013; 477.

[4] N.S. Manam, W.S.W. Harun, D.N.A. Shri, S.A.C. Ghani, T. Kurniawan, M.H. Ismail, M.H.I. Ibrahim: Study of corrosion in biocompatible metals for implants: A review, Journal of Alloys and Compounds, 2017; 701: 698-715.

[5] J. Pellier, J. Geringer, B. Frost: Fretting-corrosion between 316L SS and PMMA: Influence of ionic strength, protein and electrochemical conditions on material wear. Application to orthopaedic implants. Wear, Elsevier, 2011; 271(9-10): 1563-1571.

[6] B. Świeczko-Żurek: Ocena struktury i własności mechanicznych oraz odporności korozyjnej tworzyw metalowych na implanty dla chirurgii kostnej, Gdańsk, 2009.

[7] K. Hee-Lyang, P. Il-Song, L. Sook-Jeong, Y. Mi-Kyung, L. Kwang-Won, B. Tae-Sung, L. Min-Ho: Effect of surface pretreatment and pack cementation on bioactivity of titanium dental implant. Surface and Coatings Technology, 2014; 259: 178-184.

[8] H. Tan, S. Guo, S. Yang, X. Xu, T. Tang: Physical characterization and osteogenic activity of the quaternized chitosan-loaded PMMA bone cement. Acta Biomaterialia, 2012; 8(6): 2166-2174.

[9] S. Y. Kim, S. H. Jeon: Setting properties, mechanical strength and evaluation of calcium phosphate-based bone cements. Journal of Industrial and Engineering Chemistry, 2012; 18(1): 128-136.

[10] M. Miola, A. Bistolfi, M. C. Valsania, C. Bianco, G. Fucale, E. Verné: Antibiotic-loaded acrylic bone cements: An in vitro study on the release mechanism and its efficacy. Materials Science and Engineering: C, 2013; 33(5): 3025-3032.

[11] PN-EN ISO 10993-15.

[12] J. Loch, H. Krawiec: Corrosion behaviour of cobalt alloys in artifical salvia solution, Arch. Foundry Eng., 2013; 13: 101–106.