QUALITY CONTROL BASE ON SURFACE ROUGHNESS CHARACTERISTIC – OXIDE LAYER ON PURE TITANIUM

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Abstract

Titanium, invariably for decades, is the most promising metallic material used in medicine (implantology). And its suitability is primarily determined by biotolerance, which depends on the preparation of the surface of the elements. This paper assesses the quality control of oxide layers produced on pure (medical) titanium in the process of thermal oxidation in an air atmosphere. The parameters characterizing surface roughness have been used as control parameters. It was noted that the titanium surface undergoes a slight change with short oxidation times, and the oxidation is relatively even in nature. However, with longer oxidation times (more than 45 minutes) roughness parameters change drastically, which is not always beneficial from the point of view of further use.

Keywords: Quality control, titanium oxidation, oxide layer, roughness

1. INTRODUCTION

Titanium and its alloys are a group of metallic materials that enjoy the greatest interest in medicine, especially in implantology [1,2]. Titanium owes this special distinction to the medical industry: relatively low specific gravity (density), very satisfactory ratio of strength to density or yield strength, very good strength in fatigue tests, among metallic biomaterials the lowest value of Young's modulus, but most importantly biotolerance, tendency to spontaneous passivation, high local and general corrosion resistance [3–7]. Intensive development of the industry (especially medical industry), the search for new solutions, an effort to implement the principles of Industry 4.0 and sustainable development [8, 9], invariably based on the proper and thorough knowledge of mechanisms occurring spontaneously (or without human ingerention) - often such processes are called special processes, of which the assessment quality is particularly difficult and requires the use of destructive testing and statistical analysis [10]. Despite the very satisfactory properties of pure titanium, research (based on basic knowledge) to improve its properties is constantly carried out. Pure titanium easily passivates with minimal oxygen or moisture content in the operating environment - the result of the spontaneous oxidation process is an oxide layer consisting mainly of TiO_2 (rutile, anatase) [11–13]. There are many technologies to improve the performance of titanium, addition in biomedical composites [14], alloying [15,16]- the most commonly used implants are made of titanium alloys. There are also a number of technologies for surface modification of Ti or alloy elements, e.g. production of conversion layers ($Ti(HPO_4)_2 \cdot nH_2O$), nitriding [17], application of substoichiometric oxide layers (tribofilms like γ-Ti_3O_5, Ti_5O_9 and Ti_9O_{17} and $Mo_{0975}Ti_{0025}O_2$ as well as double oxides, like β-$NiMoO_4$ or $NiTiO_3$) [18], etc. However, the most common method for surface treatment of titanium-based metals is thermal or electrochemical oxidation [4,7,13,19]. This article attempts to characterize and identify the quality of oxide layers formed on pure titanium during thermal oxidation in an air atmosphere. Couse that the main limitation in the use of pure titanium is its poor resistance to abrasive wear, as a result of oxide layer damaged or deformation [7,11], the set of surface roughness parameters has been used as parameters for verifying the quality of titanium oxide layer.

The issue discussed in this article may be of interest in many other areas, including bioceramics layers [20], a behavior of the layer [21] and its corrosion resistance [22,23], what may be of significance interest in biotechnology [24,25]. Such results should be also taken into consideration in evaluation methodologies [26, 27] and decision processes [28-30] as well as in the stereological analysis [31-33], laser machining of surface layers [34-36] and uncertainty analysis [37].

2. EXPERIMENTAL

As tested material commercial, technically pure titanium Grade 2 (Bibus Metals) has been used. Titanium Grade 2 is one of the most commonly used variants of titanium in implantology. The sample before exposure in oxidation atmosphere were polished on water paper with gradation to 1000, then rinsed with distilled water, degreased with methyl alcohol. 13 series of samples were prepared (10 in each series). All samples have been placed in an oven chamber (with free atmosphere access to the measured surface). Oxidation has been carried out at 700±30 °C. Oxidation time has been measured from the moment the stated temperature was reached. Pure titanium samples oxidized for 5, 10, 15, 20, 30, 35, 40, 45, 50, 60, 90 and 120 minutes. Sample 0 was used as reference (no oxidation, roughness determined immediately after grinding and degreasing

The 2D roughness measurement has been performed using a contact profilometer (MarSurf PS 10). Measurement of roughness parameters have been carried out in accordance with the standard ISO 13565-2, the measuring section 4 mm. Five measurements have been made on each sample. Data presented in the paper is the arithmetic mean of all measurements for samples from one series. According ISO standard (ISO 13565-2) during measurements the fallowing parameters have been determined: Ra - arithmetic mean deviation of the assessed profile, Rz - maximum height of the profile, Rp - maximum profile peak height, Rv - maximum profile valley depth, Rt - total height of the profile, Rk - core roughness depth.

3. RESULTS AND DISCUSSION

The results of the parameters measurements (average value with standard deviation) have been presented in **Table 1**.

Table 1 Selected, most important surface roughness parameters determined for titanium after thermal oxidation in air atmosphere (700 °C) with exposure time range from 0 to 120 minutes

Time, min	Roughness parameters, µm					
	Ra	Rz	Rmax	Rp	Rv	Rt
0	0.146	1.465	2.090	0.701	0.764	2.090
5	0.177	1.440	1.739	0.686	0.754	1.739
10	0.201	1.978	2.405	0.708	1.269	2.507
15	0.202	1.802	2.172	0.634	1.168	2.192
20	0.244	2.430	2.960	0.751	1.679	3.201
30	0.325	2.874	3.728	0.784	2.090	3.728
35	0.356	3.019	3.581	1.019	2.001	3.835
40	0.639	5.461	8.155	1.457	4.004	8.299
45	0.863	7.277	9.660	1.522	5.755	9.660
50	0.858	7.749	9.128	1.430	6.319	9.391
60	0.823	7.860	9.170	1.440	6.016	10.328
90	0.963	7.777	9.120	1.502	6.075	9.860
120	0.938	7.749	9.280	1.453	6.318	9.481

In **Figure 1** the most representative surface roughness profiles for a titanium after surface oxidation have been shown. In **Figure 1** are presented the representative profiles for a sample 0 (no treatment, after grinding and polishing), and then for the samples after thermal oxidation during 5, 40 and 120 minutes of exposure. Profile images have been crated using standard compliant filters (ISO 16610-21 and ISO 13565-2).

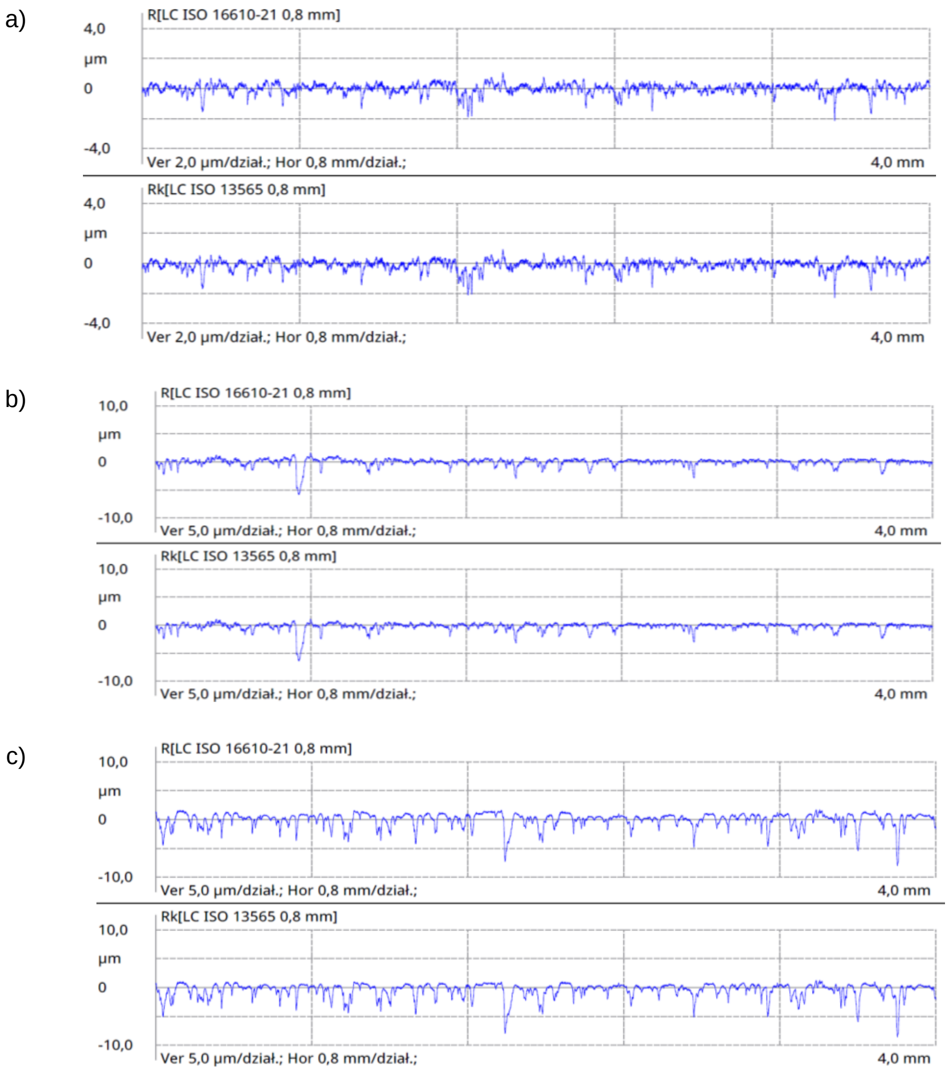

Figure 1 The representative profiles for a sample after thermal oxidation:
a) 5, b) 40 and c) 120 minutes of exposure

As is easily seen, on the roughness profiles in the initial oxidation phase (at short times up to 20 minutes), the surface roughness changes significantly. The profile has numerous peaks, hills, valleys and pits - and the oxidation is even. However, with longer spontaneous thermal oxidation times, considerable surface variation is observed and visible valleys and pits appear on the profile - much less peaks (than pits) are observed (Rp), which may mean that the oxide layer no longer increases, oxidation processes occur in deeper part of the surface layers, which causes damage and cracks in the topmost oxide layer. This also may be evidence of a gradual peeling of the oxide layer (Rv).

Based on the data presented in **Table 1** the graphs representing changes of surface roughness parameters have been prepared - **Figure 2**. The most important parameter Ra of the assessed profile – has been used to define the random surface roughness (stochastic) in some measurable space. Ra is used as a global evaluation of the roughness amplitude on a profile.

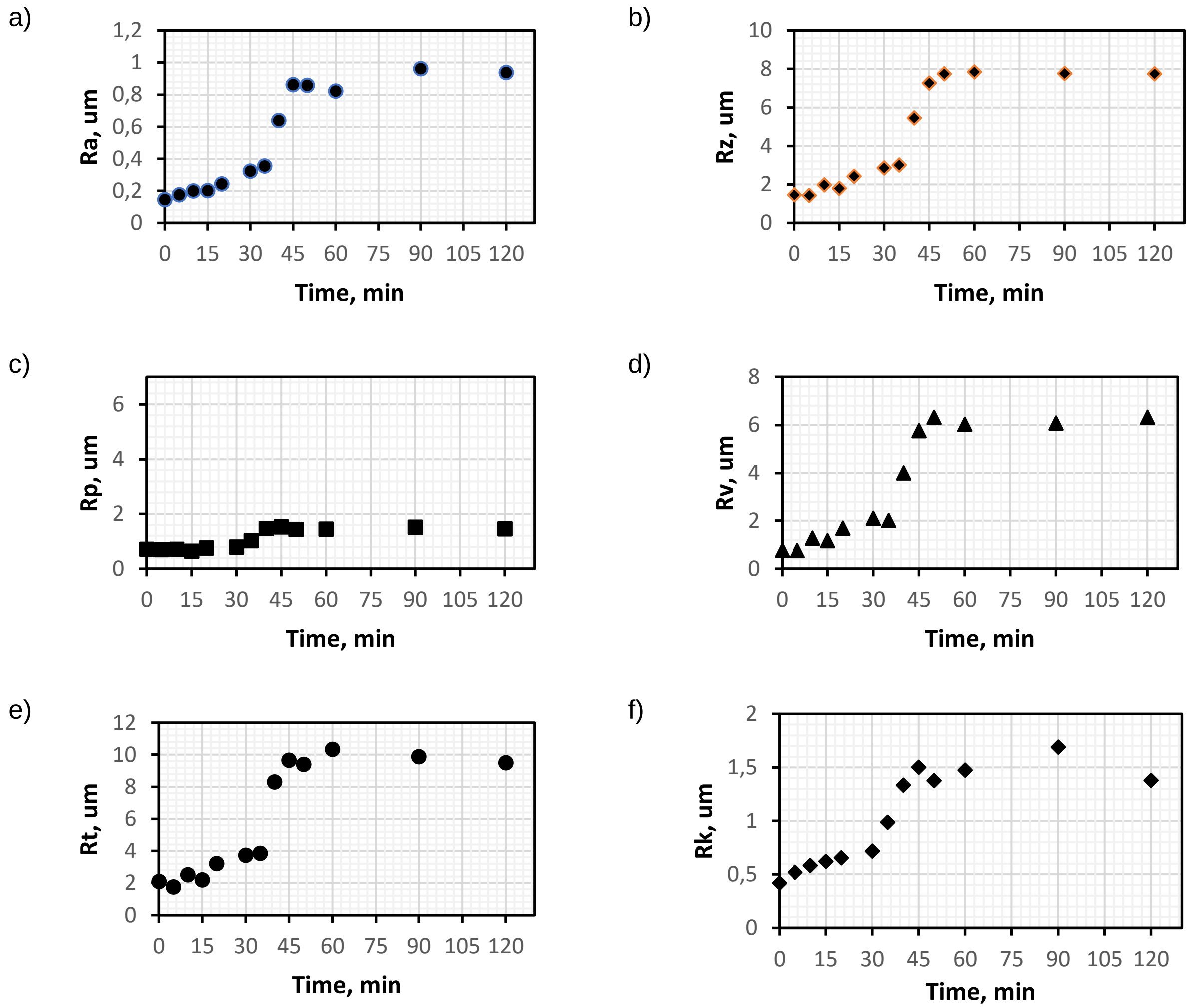

Figure 2 Change in sourface roughness parameters as a function of thermal oxidation time: a) Ra, b) Rz, c) Rp, d) Rv, e) Rt, f) Rk – surface of pure titanium after thermal oxidation

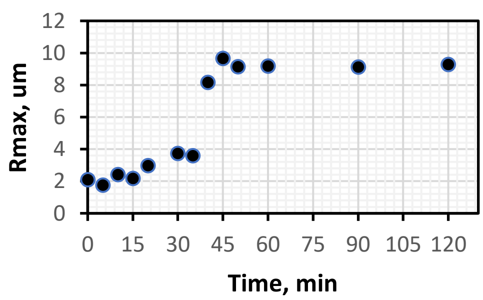

Figure 3 Change in Rmax (sourface roughness parameter) as a function of thermal oxidation time – surface of pure titanium after thermal oxidation

As can be easily seen, the short exposure times (5, 10 minutes) of the pure titanium in oxidizing atmosphere have only a slight effect on the change in surface roughness. Clear changes are observed at times above 30 minutes. In this case, the Ra parameter value increases even 3 times. Longer exposure times (over 50 minutes) strongly change the parameter, but it is observed that running the process for more than 50 minutes does not make sense, as there are clearly no major changes on the metal surface. The value of the Ra parameter is at a comparable level. In addition, it can be observed that the Rmax value (maximum deviation from the average line) increases significantly, which may indicate a selective effect of the oxidation or the formation of defects on the oxide layer and surface cacking (**Figure 3**).

4. CONCLUSION

Based on the presented results about the assessment of the quality of the oxide layer on titanium (after thermal oxidation in the air atmosphere) it can be stated that with short oxidation times, the titanium surface undergoes a slight change, and the oxidation is relatively even in nature - the value of most parameters (including mainly Ra) slightly increases. However, with longer oxidation times (more than 45 minutes), roughness parameters change drastically - all parameters increase drastically, but there are definitely more valleys than the peaks visible on the roughness profile - the Rv parameter increases significantly**,** which may indicate a selective effect of the oxidation or the formation of defects on the oxide layer and surface cracking.

REFERENCES

[1] KAZEK-KĘSIK, A., NOSOL, A. and PŁONKA J. Physico-chemical and biological evaluation of doxycycline loaded into hybrid oxide-polymer layer on Ti-Mo alloy. *Bioactive Matererials.* 2020. vol. 5, pp. 553–63.

[2] BRUNETTE, D.M., TENGVALL, P., TEXTOR, M. and THOMSEN, P. (eds.) *Titanium in Medicine.* Berlin Heidelberg: Springer Verlag 2001.

[3] KONEČNÁ R., MEDVECKÁ, D. and NICOLETTO, G. Structure, Texture and Tensile Properties of Ti6Al4V Produced by Selective Laser Melting. *Production Engineering Archives.* 2019. vol. 25, pp. 60–65.

[4] KLIMECKA-TATAR, D., BORKOWSKI, S. and SYGUT, P. The kinetics of Ti-1Al-1Mn alloy thermal oxidation and characteristic of oxide layer. *Arch. Metall. Mater.* 2015. vol. 60, pp. 735–38.

[5] CHOJNACKA, A., KAWALKO, J., KOSCIELNY, H. et al. Corrosion anisotropy of titanium deformed by the hydrostatic extrusion. *Applied Surface Science.* 2017. vol. 426, pp. 987–94.

[6] ANIOŁEK, K. and KUPKA, M. Mechanical, tribological and adhesive properties of oxide layers obtained on the surface of the Ti–6Al–7Nb alloy in the thermal oxidation process. *Wear.* 2019, pp. 432-433, 202929.

[7] KLIMECKA-TATAR, D. Electrochemical characteristics of titanium for dental implants in case of the electroless surface modification. *Arch. Metall. Mater.* 2016. vol. 61, pp. 923–26.

[8] KLESZCZ, D., ZASADZIEŃ, M. and ULEWICZ, R. Lean Manufacturing in the ceramic industry. *Multidisciplinary Aspects of Production Engineering.* 2019. vol. 2, pp. 457–66.

[9] INGALDI, M. and ULEWICZ, R. Problems with the Implementation of Industry 4.0 in Enterprises from the SME Sector. *Sustainability.* 2020. vol. 2, art. 217.

[10] ULEWICZ, R. and MAZUR, M. Economic Aspects of Robotization of Production Processes by Example of a Car Semi-trailers Manufacturer. *Manufacturing Technology - Engineering Science and Research Journal.* 2019. vol.19, pp.1054–59.

[11] POUILLEAU, J., DEVILLIERS, D., GARRIDO, F. et al. Structure and composition of passive titanium oxide films. *Materials Science and Engineering: B*. 1997. vol. 47, pp. 235–243.

[12] GARDOS, M.N. The Effect of Anion Vacancies on the Tribological Properties of Rutile (TiO 2–x). *Tribology Transactions*. 1988, vol. 31, pp. 427-436.

[13] BHATTACHARYA, S.K., SAHARA, R., SUZUKI, S. et al. Mechanisms of oxidation of pure and Si-segregated α-Ti surfaces. *Applied Surface Science.* 2019, vol. 463. pp. 686–692.

[14] DUDEK, A. and KLIMAS, M. Composites based on titanium alloy Ti-6Al-4V with an addition of inert ceramics and bioactive ceramics for medical applications fabricated by spark plasma sintering (SPS method). *Mat.-wiss. u. Werkstofftech.* 2015, vol. 46, pp. 237-247.

[15] SZOTA, M., ŁUKASZEWICZ, A. and BUKOWSKA, A. Influence of mechanical activation and heat treatment on surface development and oxide layer thickness of Ti6Al4V ELI alloy. *Journal of Achievements in Materials and Manufacturing Engineering.* 2019. vol. 2, pp. 69–76.

[16] SZOTA, M., LUKASZEWICZ, A. and KOSINSKI, K. *The Influence of Parameters of Heat Treatment on Thickens and Roughness of Oxide Layers on Titanium Alloy Ti6Al4V*. *Revista Chimie*. 2018. vol. 69, pp. 2850–2853.

[17] JAGIELSKA-WIADEREK, K., BALA, H. and WIERZCHON, T. Corrosion depth profiles of nitrided titanium alloy in acidified sulphate solution. *Central European Journal of Chemistry.* 2013. vol. 11, pp. 2005-2011

[18] WOYDT, M. Sub-stoichiometric oxides for wear resistance. *Wear.* 2019. vol. 440-441, art. 102735.

[19] ANIOŁEK K., KUPKA M. and DERCZ G. Cyclic oxidation of Ti–6Al–7Nb alloy. *Vacuum.* 2019. vol. 168, art. 108859.

[20] DUDEK, A. and WLODARCZYK, R. Structure and Properties of Bioceramics Layers Used for Implant Coatings. *Solid State Phenomena*. 2010, vol. 165, pp. 31-36.

[21] KORZEKWA, J., BARA M., PIETRASZEK, J. and PAWLUS, P. Tribological behaviour of Al2O3/inorganic fullerene-like WS2 composite layer sliding against plastic. *Int. J. Surf. Sci.Eng.* 2016, vol. 10, pp. 570-584.

[22] SZABRACKI, P. and LIPINSKI, T. Influence of sigma phase precipitation on the intergranular corrosion resistance of X2CrNiMoN25-7-4 super duplex stainless steel. In *METAL 2014: 23rd Int. Conf. Metallurgy and Materials*. Ostrava, TANGER, 2014, pp. 476-481.

[23] LIPINSKI, T. Double modification of AlSi9Mg alloy with boron, titanium and strontium. *Arch. Metall. Mater*. 2015, vol. 60, pp. 2415-2419.

[24] SKRZYPCZAK-PIETRASZEK, E., PISKA, K. and PIETRASZEK, J. Enhanced production of the pharmaceutically important polyphenolic compounds in Vitex agnus castus L. shoot cultures by precursor feeding strategy. *Engineering in Life Sciences*. 2018. vol. 18, pp.287-297.

[25] SKRZYPCZAK-PIETRASZEK, E., URBANSKA, A., ZMUDZKI, P. and PIETRASZEK, J. Elicitation with methyl jasmonate combined with cultivation in the Plantform™ temporary immersion bioreactor highly increases the accumulation of selected centellosides and phenolics in Centella asiatica (L.) Urban shoot culture. *Engineering in Life Sciences*. 2019. vol. 19, pp.931-943.

[26] BORKOWSKI, S. and INGALDI M. Workers evaluations of ribbed wire competition and rolling mill technological possibilities. In *METAL 2013: 22nd Int. Conf. Metallurgy and Materials*. Ostrava, TANGER, 2013, pp. 1920-1925.

[27] INGALDI, M. and ULEWICZ, R. Evaluation of Quality of the e-Commerce Service. *International Journal of Ambient Computing and Intelligence*. 2018. vol. 9, pp. 55-66.

[28] PACANA, A., PASTERNAK-MALICKA, M., ZAWADA. M. and RADON-CHOLEWA, A. Decision support in the production of packaging films by cost-quality analysis. *Przemysl Chemiczny*. 2016. vol. 95, pp. 1042-1044.

[29] MALINDZAK, D., PACANA, A. and PACAIOVA, H. An effective model for the quality of logistics and improvement of environmental protection in a cement plant. *Przemysl Chemiczny*. 2017. vol. 96, pp. 1958-1962.

[30] ULEWICZ, R. and BLASKOVA, M. Sustainable development and knowledge management from the stakeholders' point of view. *Polish Journal of Management Studies*. 2018. vol. 18, pp. 363-374.

[31] WOJNAR, L., GADEK-MOSZCZAK, A. and PIETRASZEK, J. On the role of histomorphometric (stereological) microstructure parameters in the prediction of vertebrae compression strength. *Image Analysis and Stereology*. 2019, vol. 38, pp.63-73.

[32] GADEK-MOSZCZAK, A., RADEK, N., WRONSKI, S. and TARASIUK, J. Application the 3D Image Analysis Techniques for Assessment the Quality of Material Surface Layer Before and After Laser Treatment. *Advanced Materials Research-Switz*. 2014. vol.874, pp.133-138.

[33] GADEK-MOSZCZAK, A., PIETASZEK, J., JASIEWICZ, B., SIKORSKA, S. and WOJNAR, L. The bootstrap approach to the comparison of two methods applied to the evaluation of the growth index in the analysis of the digital X-ray image of a bone regenerate. *New Trends in Comp. Collective Intell*. 2015. vol. 572, pp.127-136.

[34] RADEK, N. and BARTKOWIAK, K. Laser treatment of Cu-Mo Electro-Spark Deposited Coatings. *Physics Procedia*. 2011. vol. 12, pp. 499-505.

[35] RADEK, N. and BARTKOWIAK, K. Laser treatment of electro-spark coatings deposited in the carbon steel substrate with using nanostructured WC-Cu electrodes. *Physics Procedia*. 2012. vol. 39, pp. 295-301.

[36] SCENDO, M., TRELA, J. and RADEK, N. Influence of laser power on the corrosive resistance of WC-Cu coating. *Surface & Coatings Technology*. 2014. vol. 259, pp. 401-407.

[37] PIETRASZEK, J. and SKRZYPCZAK-PIETRASZEK, E. The Optimization of the Technological Process with the Fuzzy Regression. *Adv. Mater. Res-Switz*. 2014. vol. 874, pp. 151-155.