D.Sc. Jarosław Jan Jasiński Czestochowa University of Technology

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# **ATTACHMENT NO. 3**

# AUTOREFERAT

presenting a description of achievements and scientific or artistic achievements, in particular the achievements referred to in Article 16 sec. 2 acts of March 14, 2003

Czestochowa, April 25<sup>th</sup> 2019

- 1. Name and Surname: Jarosław Jan Jasiński
- 2. Diplomas, academic degrees with name, place and year of obtaining them and the title of the doctoral dissertation.

Academic degree: Doctor of Technical Sciences Science Discipline: Material Engineering

Czestochowa University of Technology Faculty of Production Engineering and Materials Technology Institute of Materials Engineering

Date of awarding the scientific degree: October 28th 2014, Czestochowa

Title of work: Phenomena and effects of active screen influence on ion nitriding processes (Zjawiska i efekty oddziaływania ekranów aktywnych (active screen) w procesie azotowania jonowego)

D.Sc. Thesis Supervisor: Associate Professor Tadeusz Frączek

Reviewers: Professor Andrzej Lis

Associate Professor Jerzy Robert Sobiecki

Academic degree: Master of Science

Science Discipline: Material Engineering Specialization: Protection against corrosion

# AGH University of Science and Technology Cracow, Poland Faculty of Materials Science and Ceramics,

Department of Solid State Physical Chemistry

Date of awarding the scientific degree: July 7th 2009, Cracow

Title of work: Three-dimensional interdiffusion 3D (Dyfuzja wzajemna w geometrii trójwymiarowej)

MSc Thesis Supervisor: **Professor Marek Danielewski** Reviewer: **Associate Professor Bartłomiej Wierzba**  3. Information on the previous employments in the scientific units.

01.10.2009 - 28.10.2014	D.Sc. Student
	Czestochowa University of Technology
	Faculty of Production Engineering
	and Materials Technology
03.06.2015 - 30.09.2015	R&D Research and Development Department
	Coordinator
	Narzędziownia Bogdan Pszenica
	ul. Częstochowska 1b
	46 – 320 Praszka
01.03.2015 – present	Assistant Professor
	Czestochowa University of Technology
	Faculty of Management

Institute of Logistics and International Management

- 4. Indication of the scientific achievement under Act 16 sec. 2 of the Act from March 14<sup>th</sup> 2003 on academic degrees and academic title as well as degrees and title in the field of art (Journal of Laws of 2016, item 882, as amended in Journal of Laws of 2016, item 1311):
  - a) Title of the scientific achievement

# Titanium substrates functionalization to enhance bioactivity in biomedical applications

 b) (author / authors, title / titles of the publication, year of publication, name of the publishing house, publishing reviewers),

# **Publications:**

 J.J. Jasiński, M. Lubas, Ł. Kurpaska, W. Napadłek, M.Sitarz, (2018), Functionalization of Ti99.2 Substrates Surface by Hybrid Treatment Investigated with Spectroscopic Methods, Journal of Molecular Structure, Vol.1164, 412÷419 (JCR JIF = 2.011)

My contribution to this article consisted in carrying out research, analyzing results, developing and interpreting results, writing chapters and conclusions of the manuscript. I estimate my contribution to 75%.

 M. Lubas, J.J. Jasiński, P. Jeleń, M.Sitarz, (2018), Effect of ZrO2 Sol-Gel Coating on the Ti99.2 - Porcelain Bond Strength Investigated with Mechanical Testing and Raman Spectroscopy, Journal of Molecular Structure, Vol.1168, 316÷321 (JCR JIF = 2.011)

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 30%.

 J.J. Jasiński, Ł. Kurpaska, M. Lubas, M. Leśniak, J. Jasiński, M. Sitarz, (2016), Effect of hybrid oxidation on the titanium oxide layer's properties investigated by spectroscopic methods, Journal of Molecular Structure, 1126, 165÷171 (JCR JIF = 1.753)

My contribution to this article consisted in carrying out research, analyzing results, developing and interpreting results, writing chapters and conclusions of the manuscript. I estimate my contribution to 75%.

 J.J. Jasiński, Ł. Kurpaska, M. Lubas, J.Jasiński, M. Sitarz, (2016), Duplex Titanium Oxide Layers for Biomedical Applications, ASTM Materials Performance and Characterization, Vol. 5, No 4, 461÷471

My contribution to this article consisted in carrying out research, analyzing results, developing and interpreting results, writing chapters and conclusions of the manuscript. I estimate my contribution to 75%.

 M. Lubas, J.J. Jasiński, M.Sitarz, Ł.Kurpaska, P.Podsiad, J.Jasiński, (2014), Raman Spectroscopy of TiO2 Thin Films Formed by Hybrid Treatment for Biomedical Applications, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol.133, 867÷871 (JCR JIF = 2.353)

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 45%.

 M. Lubas, M. Sitarz, J.J. Jasiński, P.Jeleń, L. Klita, P. Podsiad, J. Jasiński, (2014), Fabrication and Characterization of Oxygen - Diffused Titanium Using Spectroscopy Method, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol.133, 883÷886 (JCR JIF = 2.353)

My contribution to this article consisted in the analysis of results, the development and graphic interpretation of results, the writing of manuscript chapters and conclusions. I estimate my contribution to 40%.

 M.Lubas, P.Podsiad, J.J. Jasiński, J.Jasiński, M.Sitarz, (2014), Właściwości tribologiczne tytanu po procesie utleniania w złożu fluidalnym, Inżynieria Materiałowa, R.35, Nr 5 (201), 393÷396

My contribution to this article consisted in the analysis of results, the development and graphic interpretation of results, the writing of manuscript chapters and conclusions. *I estimate my contribution to* 35%.

 J. Jasiński, B. Rajchel, M. Lubas, J.J. Jasiński, B. Kucharska, P. Podsiad, (2013) Investigation of TiO2 Thin Coatings for Medical Applications by X-Ray Diffraction and Raman Microspectroscopy, Solid State Phenomena, Vols. 203-204, 165÷168

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 50%.

 J. Jasiński, M. Lubas, J.J. Jasiński, P. Wieczorek, (2013), Titanium Oxidation Effects After Various Surface Modification Methods, Engineering of Biomaterials, Vol.16, R.16, No 120, 41÷47

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 35%.

 J. Jasiński, M. Lubas, J.J. Jasiński, P. Podsiad, J. Gawroński, L. Jeziorski, (2013), Aktywowanie warstwy wierzchniej Ti Grade 2 w procesach utleniania, Inżynieria Materiałowa, Nr 5 (195), R.34, 455÷458

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. . I estimate my contribution to 45%.

 T. Frączek, J.Jasiński, M. Olejnik, J.J. Jasiński, A. Skuta, (2012), Tlenoazotowanie jonowe tytanu Grade 2 metodą active screen (AS), Inżynieria Materiałowa, Nr 3 (187), R.33, 173÷176

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 75%.

 J. Jasiński, P. Podsiad, J.J. Jasiński, M.Lubas, (2012), Właściwości warstwy wierzchniej tytanu Grade 2 po utlenianiu w złożu fluidalnym, Inżynieria Materiałowa, R.33, Nr 5 (189), 366÷369

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 45%.

T. Frączek, L. Jeziorski, M. Olejnik, J.J. Jasiński, (2010), Analiza profilowa tytanu Grade 5 po procesie azotowania jarzeniowego, Inżynieria Materiałowa, Nr 4(176), R.31, 957÷960

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 40%.

14. T. Frączek, M.Olejnik, **J.J.Jasiński**, (2010), Warstwa wierzchnia stopów tytanu po azotowaniu jarzeniowym, **Inżynieria Powierzchni**, **Nr 2, 69÷73** 

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 33%.

 T. Frączek, M. Olejnik, J.J. Jasiński, (2010), Warstwa wierzchnia tytanu po niekonwencjonalnym azotowaniu jarzeniowym, Inżynieria Materiałowa, R.31, nr 4(176), 961÷964

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. I estimate my contribution to 33%.

 T. Frączek, M. Olejnik, J.J. Jasiński, (2010), Warstwa wierzchnia tytanu po niekonwencjonalnym azotowaniu jarzeniowym, Inżynieria Materiałowa, R.31, nr 4(176), 961÷964

My contribution to this article consisted in the analysis of results, the elaboration and graphic interpretation of results, the writing of manuscript chapters. . I estimate my contribution to 33%.

# Patents and patent applications

17. **Patent PL nr 221053**, Method for modifying the surface layer of titanium alloy implants, P.Podsiad, **J.J. Jasiński**, J.Jasiński, R. Czyż

My contribution to the creation of the patent consisted in the implementation of induction titanium oxidation processes in steam and preparation of a patent description. I estimate my contribution to 25%.

 Patent application no. Pat-24/05/07/12, Method of thermo-chemical treatment of metals and metal alloys, J. Jasiński, P. Podsiad, J.J. Jasiński application date 05.07.2012

My contribution to the creation of the patent was based on the implementation of hybrid titanium oxidation processes and the preparation of a patent application. I estimate my contribution to 33%.

### Completed projects and constructional achievements

 P. Podsiad, J.J. Jasiński, J. Jasiński, R. Czyż, Development and execution of a laboratory stand for the implementation of titanium induction steam oxidation processes for patent application (Patent PL no. 221053) – pkt. I.B). 17 – attachment No. 4)

My contribution to the creation of a laboratory stand consisted in developing documentation for the induction heating system and the steam generating system. I estimate my contribution to 30%.

# Conference materials abstracts, posters, plenary papers included in the scientific achievement

- 20. J.J. Jasiński, (2018), Titanium oxide duplex hybrid layers for biomedical applications NOVATHERM 3 Innovative Solutions in Heat Treating Seminar, Piekary Śląskie 03-05 10.2018 plenary speech My contribution to the creation of this work consisted in the development of results and presenting the paper. I estimate my contribution to 100%.
- J.J. Jasiński, (2017), Low-emission techniques in surface engineering in terms of environmental and operational conditions improvement in the metalworking sector – hybrid treatment of titanium, International Scientific Conference Chemical Safety and Health Protection, AGH Cracow 10-11.10. 2017 – plenary speech

My contribution to the creation of this work consisted in the development of results and presenting the paper. I estimate my contribution to 100%.

22. J.J. Jasiński, M.Lubas, Ł. Kurpaska, W.Napadłek, M.Sitarz, (2017), Spectroscopic Investigation of Titanium Based Functional Materials Formed with Different Hybrid Treatments, XIVth International Conference on Molecular Spectroscopy, Białka Tatrzańska 3÷7 september, 2017, p.171 – poster presentation

My contribution to the creation of this work consisted in the development of results and presenting the poster. I estimate my contribution to 55%.

 M. Lubas, J.J. Jasiński, Ł. Kurpaska, E. Długoń, M. Sitarz, (2017) Titanium -Bioceramics Sol-Gel Layer Interface Bond Strength Investigation with Mechanical Testing and Raman Spectroscopy, XIVth International Conference on Molecular Spectroscopy, Białka Tatrzańska 3÷7 september 2017,Book of Abstracts p.172 – poster presentation

My contribution to the creation of this work consisted in the development of results and presenting the poster. I estimate my contribution to 40%.

24. J.J. Jasiński, T. Frączek, M. Lubas, Ł. Kurpaska, J. Jasiński, M. Sitarz, (2017) Hydroxyapatite Molecules Formation on Titanium 99.2 Substrates after Duplex/Hybrid Treatment, XIVth International Conference on Molecular Spectroscopy, Białka Tatrzańska 3÷7 września 2017, Book of Abstracts p.169 – poster presentation

My contribution to the creation of this work consisted in the development of results and presenting the poster. I estimate my contribution to 55%.

25. J.J. Jasiński, Ł. Kurpaska, M. Lubas, M. Leśniak, J. Jasiński, M. Sitarz, (2015), Effect of hybrid oxidation on the titanium oxide layer's properties investigated by spectroscopic methods, XIIIth International Conference on Molecular Spectroscopy ICMS 2015 09-13.09.2015 Wrocław – poster presentation

My contribution to the creation of this work consisted in the development of results and presenting the poster. I estimate my contribution to 55%.

 M.Lubas, M.Leśniak, J.J. Jasiński, J.Jasiński, E.Długoń, M.Sitarz, (2015), Wpływ obróbki powierzchniowej na siłę połączenia tytan-porcelana stomatologiczna, XII Ogólnopolska Konferencja Naukowa "Tytan i jego stopy - 2015", Zawiercie 11÷14 października 2015, Spis streszczeń s.48 – poster presentation

*My* contribution to the creation of this work consisted in the elaboration and writing of an abstract. *I* estimate my contribution to 40%.

 M. Lubas, J.J. Jasiński, J.Jasiński, P.Jeleń, L. Klita, (2013), Fabrication and Characterization of Oxygen-Diffused Titanium by Raman Spectroscopy Method, XIIth International Conference on Molecular Spectroscopy. From Molecules to Nano- and Biomaterials, 8÷12 September, Kraków - Białka Tatrzańska, 2013, p.191 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

 J. Jasiński, M. Lubas, J.J. Jasiński, P. Wieczorek, (2013), Titanium oxidation effects after various surface modification methods, Miedzynarodowa Konferencja Naukowa Biomaterials in Medicine and Veterinary Medicine 2013, Rytro, 10÷13.10.2013 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

29. B. Rajchel, J. Jasiński, E. Proniewicz, W. Kowalski, P. Strączek, M. Lubas, J.J. Jasiński, (2013), Raman Microspectroscopy of the Amorphous C(Ti) Coatings Formed with Selected Ionic Methods on Titanium and UHMWPE, XIIth International Conference on Molecular Spectroscopy. From Molecules to Nano- and Biomaterials, 8÷12 september 2013, Kraków - Białka Tatrzańska, Book of Abstacts p.185 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

30. P. Podsiad, M. Lubas, M. Sitarz, J. Jasiński, J.J. Jasiński, P. Jeleń, Ł. Klita, Ł. Kurpaska, (2013), Raman Spectroscopy of TiO2 Thin Films Formed by Hybrid Treatment for Biomedical Applications, XIIth International Conference on Molecular Spectroscopy. From Molecules to Nano- and Biomaterials, 8÷12 september 2013, Kraków - Białka Tatrzańska, Book of Abstacts p. 199 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 30%.

31. J. Jasiński, M. Lubas, J.J. Jasiński, P. Podsiad, J. Gawroński, L. Jeziorski, (2013), Aktywowanie warstwy wierzchniej Ti Grade 2 w procesach utleniania,
V Ogólnopolska Konferencja Naukowa Nowoczesne Technologie w Inżynierii Powierzchni Łódź – Spała 18÷21.09.2013 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

32. J. Jasiński, B. Rajchel, P. Podsiad, J.J. Jasiński, M. Lubas, B. Kucharska, (2012), Investigation of TiO2 Thin Coatings for Medical Applications by X-ray Diffraction and Raman Microspectroscopy, XXII Conference on Applied Crystallography, 2÷6 september, Targanice 2012, Book of Abstracts 97÷98 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

33. B. Rajchel, J.J. Jasiński, P. Podsiad, J. Jasiński, (2012), Raman Microspectroscopy of TiO2 Thin Coatings for Medical Applications Formed in Fluidized Bed, SemPiSC. XII Seminarium Powierzchnia i Struktury Cienkowarstwowe, 9÷12 may, Szklarska Poręba, 2012, Book of Abstacts p.1 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

34. B. Rajchel, J. Jasiński, E. Proniewicz, L. Jeziorski, J.J. Jasiński, (2012), Amorphous (a-C:Ti) coatings formed by dual beam IBAD method, SemPiSC, XII Seminarium Powierzchnia i Struktury Cienkowarstwowe, Szklarska Poręba, 2012

*My* contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

35. T. Fraczek, J. Michalski, M. Olejnik, J.J. Jasinski, (2012), Mechanism of Ti99.2 titanium unconventional ion nitriding, 13th International Conference on Plasma Surface Engineering PSE 2012, 10÷14.09.2012, European Society of Thin Films, Garmisch-Partenkirchen, Niemcy – poster presentation

*My* contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

36. J.Jasiński, P.Podsiad, J.J.Jasiński, M.Lubas, (2012), Właściwości warstwy wierzchniej tytanu Grade 2 po utlenianiu w złożu fluidalnym, NMNT 2012. V Krajowa Konferencja Nowe Materiały - Nowe Technologie w Przemyśle Okrętowym i Maszynowym, 28÷31 maja 2012, Międzyzdroje, Spis streszczeń s. 97 – poster presentation

My contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 40%.

37. J.J. Jasiński, M. Olejnik, T. Frączek: Odporność tribologiczna tytanu Grade 2 po azotowaniu jarzeniowym, Nowe Technologie i Osiągnięcia w Metalurgii i Inżynierii Materiałowej, XI Międzynarodowa Konferencja Naukowa, Częstochowa 2010 – poster presentation

*My* contribution to the creation of this work consisted in the elaboration and writing of an abstract and presenting the poster. I estimate my contribution to 35%.

c) Description of the scientific / artistic purpose of the above work / work and results achieved, discussing their possible use.

#### INTRODUCTION

Nowadays, the increasingly common problem associated with the statistical extension of the society's life is to ensure the comfort of life, which entails the need to search for new solutions in the field of biomedicine and implantology to ensure the possible greatest biocompatibility and beneficial mechanical properties of the implants used. Issues including improvement of chemical activity of metallic materials used in implantology and biomedicine, mainly in the regeneration and replacement of bone tissue, are of significant application importance due to the elimination of toxic interactions of bone tissue of living organisms with physiological fluids during the operation

of implants. For many years, engineering material that occupies a special place in the field of bioengineering is titanium and its alloys. The wide application of titanium is associated with its unique mechanical properties and good corrosion resistance and biotolerance. The use of titanium for dental implants or elements of endoprostheses cooperating with the living organism allows to eliminate the risk associated with the harmful effects of alloying elements (Co, Cr, Ni) occurring in other metallic materials (steels, special alloys, etc.). Initially, it was pointed out in the literature that that metallic titanium is indifferent to the body [1]. However, in direct contact the metallosis phenomenon undergoes the tissues of organisms, which consists in the release of metal ions to the organism. This results in the occurrence of edema and inflammation, and as a result, it leads to the recoil of the implant, which is associated with patients' health problems and costs. It was also found that the biocompatibility of titanium is largely related with the physicochemical properties of the implant surface, i.e. with the formation of a passive oxide film, due to the high chemical affinity of titanium to oxygen. Thin oxide coating  $TiO_2$  is formed already at room temperature, it is stable and adheres well to the substrate but it is often too thin. However, at high temperatures, titanium oxidizes rapidly, resulting in a thicker oxide coating that is often adhesively weakly bounded to the substrate and it is exfoliated and cracked. It is also worth emphasizing that the oxide coating on the surface of titanium also ensures, in the case of bone implants, an improvement in the process of osseointegration, that is, the coalescence of the tissue with the titanium implant. Therefore, the oxidation of titanium for biomedical applications is still a challenge for biomedical engineering in obtaining both good mechanical and physicochemical properties of thin oxide films as well as the required good adhesion to the substrate. The challenge is to develop new technologies for modifying the structure and surface of titanium, improving its corrosion resistance, and in particular improvement of the strength properties of coatings and bioactivity of titanium substrates [2,3]. In the currently used technologies, the above-mentioned coatings can be obtained, among others, using methods: electrochemical, electric discharge, plasma PVD and laser methods (laser ablation, laser texturing) or by diffusion saturation of the titanium surface layer with oxygen, e.g. in a fluidized bed [4-8]. The essence of each of the mentioned methods is to create a TiO2 layer characterized by a compact and tight structure, high electrochemical and thermodynamic stability and the ability to repassify after damage in the presence of a corrosive environment. The authors of a number of works have paid great attention to the influence of the parameters of the oxidation process, including temperature, process time, oxidizing medium, pressure, etc. They found two oxidation mechanisms in the temperature range of 300 ÷ 550°C [9]. At a temperature lower than 550°C, a stoichiometric rutile coating is formed on the surface of titanium, and under it a titanium zone enriched with oxygen, but with a very rapid change in the profile of its concentration. However, at a temperature of 550°C and higher, the diffusion of oxygen in the substrate begins to play the dominant role during the oxidation process, which increases its concentration at a much greater distance from the surface and favors the relaxation of the oxygen concentration profile in the layer. Comparing the oxidation of titanium in a chamber furnace with oxidation by means of PVD methods (plasma oxidation, plasma nitriding),

slight differences in the oxidation effects were found. In both cases at the temperature of  $700^{\circ}$ C similar oxide coatings were produced on the surface well-adhered to the substrate, consisting of TiO<sub>2</sub> and TiN<sub>x</sub>O<sub>y</sub>.

In the presented scientific achievement, low-temperature processes were also carried out, mainly plasma oxynitriding and nitriding of titanium substrates in order to verify the possibility of using such processes in biomedical conditions. The main goal of the ion processes was to determine the effect of ion activation of the substrate on the possibility of maximum reduction of the saturation temperature of the titanium surface layer with nitrogen and oxygen to obtain abrasion resistant, homogeneous and dense layers of titanium nitrides with good anti-corrosion properties. The research carried out also determined the model of titanium saturation with nitrogen and oxygen and the parameters of the most beneficial processes for bio-medical applications were indicated. During the research, it was shown that the controlled conditions for conducting the ionic activation of substrates allow to control the growth of nitrides and oxides layer and allow to reduce the time of titanium saturation with nitrogen and oxygen. In the research, the processes were carried out using the innovative method of plasma oxynitriding with the use of the so-called active screen method. It was found that the use of active screens in the process allows obtaining favorable morphologies of the surface of substrates in the context of biomedical applications. Realized research and obtained results were an inspiration to explore the subject of the treatment of titanium substrates for the improvement of biomedical properties using various methods (nitriding, nitriding, plasma oxidation, fluidized bed etc.), as well as to improve the implementation of titanium activation processes before heat treatment using both mechanical methods and plasma. The achievement is therefore the next stage of research the production of substrates with controlled physicochemical properties and allows to determine the effect of the surface activation type on the processes of titanium saturation with oxygen and then the target to obtain biofunctional properties, mainly bioactivity [annex 4 B.J12., B.J8. annex 3. pos. 4.B12, 4.B14-4.B16].

Most often, in addition to plasma methods, for titanium and its alloys oxidation processes retort devices with controlled atmosphere and electrochemical methods are used. Mechanism and the kinetics of oxidation in retort devices was developed by S. Król, whereas in electrochemical methods J. Marciniak, and in the plasma-vacuum methods by T. Wierzchoń et. al [13-15]. Oxide coatings obtained by these methods are characterized by low thickness, and in the case of electrochemical coatings, not always good adhesion, which is also related to the preparation of the surface of oxidized titanium. The analysis of issues related to the use of titanium in biomedicine after the oxidation process with good properties is characterized by coatings obtained by diffusion methods, among others using a fluidized bed oxidation process. Proper selection of pre-treatment parameters (surface activation) and oxidation parameters, including fluidizing medium, temperature, atmosphere flow significantly affects the intensification of processes taking place on the surface of titanium, increasing the diffusion of oxygen to its surface layer, creating an oxide coating with good adhesion, favorable system stresses and a gentle change of concentration at the boundary of the oxide layer / diffusion

zone. It is therefore appropriate to produce an oxide coating to ensure adhesion with the maximum stress reduction between the coating and the top layer and the formation of a surface layer about the best operational parameters [pos. 4.B9, 4.B12, 4.B14]. Titanium oxidation processes are thermally activated, therefore consideration of the kinetics of the process of saturating the surface layer with oxygen and determination of the nucleation force of TiO<sub>2</sub> oxide coatings as well as assessment of changes in mechanical, physical and chemical properties of the obtained coatings creates conditions for comprehensive evaluation of phenomena and mechanisms of Ti oxidation processes. Knowledge of the mechanism of oxidation of titanium for the assessment of the most important stages of the phenomena leading to the generation of active centers allowed in the presented achievement, on the one hand, to shorten long-term processes, as well as the development of technologies combining diffusion effects with effects occurring on the surface of titanium substrates. The assumption of the conducted research related to scientific achievement is therefore to develop such a titanium substrate that would provide a "foundation" for the oxide coating with the formation of a strengthened diffusion zone of oxygen in titanium [pos. 4.B6, 4.B13]. This combination of properties of the coating and metallic substrate ensures limiting the internal stresses with good adhesion of the coating. Despite the large number of scientific and technical publications regarding technological solutions in the oxidation processes of titanium and its alloys, there are no publications that include comprehensive analysis and description of phenomena with their kinetics and mechanisms of oxidation in the mentioned technologies. This analysis should also refer to phase transitions occurring in titanium during individual processes for variable parameters (temperature, pressure, atmosphere, type of loads and stresses). For this reason, in scientific achievement, I undertook research into the analysis of individual phenomena in the process of oxidation by various technologies, including the innovative hybrid method, combining diffusion methods FADT - fluid atmopsheric diffusive treatment and PVD surface methods - magnetron sputtering, LST laser texturing - laser surface texturing, induction oxidation in steam environment - Steam-Ox, taking into account the course of the occurrences and effects of phase changes taking place in individual technologies.

#### RESEARCH OBJECTIVE AND RESULTS OF SCIENTIFIC ACHIEVEMENT

Indicated surface oxidation methods, due to the conditions of physicochemical interaction of the atmosphere with the surface, heat transfer, surface depletion, have a very limited effect on the processes of spatial oxygen diffusion in the surface layer. Therefore, it is complicated in surface treatment processes to obtain a favorable construction of zoned titanium substrates, i.e. a homogeneous, tight  $TiO_2$  oxide coating / solid  $TiO_2$  solid titanium oxide /  $Ti_{\alpha}$  core. Analysis of issues related to the use of titanium in biomedicine with good properties indicates that good strength properties have substrates obtained by diffusion methods, inter alia, using the FADT fluid bed oxidation process [pos. 4.B6]. Such oxidation of titanium as one of the methods of saturating the

surface layer provides an improvement in the strength properties of the surface layer and creates a surface of a porous oxide coating on the surface, with good corrosive properties, however, unsatisfactory bioactivity. Therefore, methods are still being sought for improving the biocompatibility of the substrate in order to achieve an increase in the intensity of the interaction of compounds with properties that support tissue regeneration (osseointegration), e.g. hydroxyapatite. The phenomenon of diffusion of oxygen to the titanium substrate in the FADT diffusion process takes place between the interstitial mechanism and the easy diffusion paths as a result of continuous defectation of the surface by the grain material of the fluidized bed (Al<sub>2</sub>O<sub>3</sub>). As a result, it helps to change the oxygen concentration profile to produce a diffusion zone of a solid oxygen solution in titanium  $Ti_{\alpha}(O)$  and a porous  $TiO_2$  titanium oxide coating in the rutile variety, with a favorable substrate-coating stress state. However, the obtained titanium substrate after fluid atmosphere diffusion FADT (fluid atmosphere diffusive treatment) with porous areas has a limited application in the aspect of improving bioactivity due to insufficient adhesion of hydroxyapatite compounds to the substrate. Therefore, research carried out in scientific achievement is aimed at producing a homogeneous, non-porous oxide coating that provides very good adhesion to biocompatible compounds. In the literature, titanium oxidation processes often include conventional saturation processes in both quasi-equilibrium (diffusion) conditions and thermodynamic imbalances (PVD, LST etc.) [16-20]. As part of the scientific achievement, two-stage hybrid oxidation processes were implemented, including diffusion in the fluidized bed (FADT) and surface oxidation (PVD, LST, Steam-Ox), in which the thermodynamic conditions of the process will interact synergistically with the substrate. The aim of the research is to develop titanium substrates whose surface zone is a diffusion saturated saturated solution of oxygen in  $Ti_{\alpha}(O)$  with high strength properties - being the foundation of the substrate, and the outer zone is a thin oxide coating  $TiO_2$  produced by selected surface methods (PVD, LST, Steam-Ox) [pos. 4.B1-4.B3]. The hybrid combination of coatings obtained, in turn, is to ensure a synergistic increase in essential properties from the point of view of the biocompatibility of the implant-tissue system. These properties are mainly the limitation of the gradient of internal stresses between the diffusion zone (FADT) of titanium saturation with oxygen, a tight and homogeneous coating obtained in the hybrid process, while improving its morphology. The combination of methods in the said hybrid system allows for a synergistic improvement of surface effects, affecting the intensity of subsequent deposition of hydroxyapatite compounds. The mentioned methods (FADT + PVD or LST or Steam-Ox) in the hybrid system allowed to use the advantages of spontaneous mechanical activation of the surface, as a result of the interaction of the fluidized bed aeromechanical medium, which is associated with continuous defect of the surface of the substrate with its simultaneous oxidation, which in turn increases the number of active centers, decides about the subsequent transport of oxygen mass to form the TiO<sub>2</sub> oxide coating (FADT process). However, the use of hybrid (non-equilibrium) surface method ensures obtaining a favorable external morphology of a thin oxide coating to improve the nucleation of biocompatible compounds (e.g. HAp), thus improving the bioactivity of titanium substrates [pos. 4.B4].

To accomplish the scope of research, I proposed the following research thesis and the purpose of the research being carried out:

# Research thesis

The use of hybrid methods for the production of oxide coatings on titanium substrates allows the creation of a synergistic substrate-coating system with the ability to control the state of the surface, to obtain a significant improvement in bioactive properties.

## Research purpose

The aim of the research is to develop processes for the hybrid treatment of titanium substrates and to evaluate the kinetics and mechanism of formation of oxide coatings, in the aspect of the surface functionalization of titanium to increase bioactive properties for biomedical applications.

The first stage of the research was to determine the effects of activation the surface of titanium intended for oxidation in a fluidized bed and hybrid methods. At this stage, metallographic analyzes of titanium microstructure were carried out in the delivery state and compared with stereometric features of titanium after the fluidized bed oxidation process. For the hybrid oxidation research, pure Grade 2 titanium for biomedical applications according to the KOBE STEEL LTD. certificate was used in the form of rods with a diameter of Ø 20mm, in the post-saturation state. The titanium used in the oxidation studies had a single phase  $Ti_{\alpha}$  structure, where the average grain size for the tested material was approx. 16-20 µm. In addition, the results showed that the adopted oxidation processes, the grain size was for oxidation, respectively at 580°C / 22 µm, 610°C / 24 µm and at 640°C / 26 µm [pos. 4.B7, 4.B11, 4.B13].

The next stage of the research was the preparation of Grade 2 titanium surface for fluidized bed oxidation processes through mechanical activation, which consisted of grinding samples using metallographic papers with grains from 360 to 2000 and mechanical activation in the sandblasting process with various sandblast media, including Al2O3 and SiO2 with a grain size of 110 µm. Sand blasting was also performed using sandblasting mixtures by appropriate selection of sanding media compositions, including, inter alia, Al2O3 + NaAl + Si3O8 + ZrO2 + TiO2 mixture. Chemical activation with the use of HF acid solutions and mixtures of HCI + HNO3 in a ratio of 3:1 and mechanicalchemical activation of Al2O3 + NaAI + Si3O8 + ZrO2 + TiO2 + H2SO4 90°C / HCl 60°C so-called. SLA - Sand blasted, Large grit, Acid etched. Activation of the surface of titanium substrates was carried out in order to modify the surface in terms of changing its surface topography and verification of beneficial activation methods in terms of obtaining diffusion surface layers and porous oxide coatings with the most beneficial properties for further hybrid processes [pos. 4.B6, 4.B9]. Analyzing the results of the surface of titanium after mechanical activation it was found that that the roughness of the surface depends to a large extent on the method used, which suggests that the activated surface is a very important factor in the production of diffusion layers and oxide coatings, and the role of the activated surface is variable with the temperature of titanium oxidation processes in the aspect

of recrystallization phenomena. On the basis of the obtained results of the surface condition, it was found that the finer particles of the sandblasting mixture used (below 110  $\mu$ m) significantly reduce the surface roughness compared to the Al<sub>2</sub>O<sub>3</sub> sandblasted surfaces, and thus lead to the formation of homogeneous, dense oxide coatings in further oxidation processes. The work also established that an additional factor activating the surface of oxidized titanium is the fluidizing aeromechanical agent, directly during the oxidation processes to the titanium substrate. Thus, fluidized bed oxidation is one of the few oxidation methods that combines the advantages of diffusion saturation with the formation of an adhesively bonded TiO<sub>2</sub> porous oxide coating.

Next, diffusion oxidation (FADT) of the titanium substrate in the fluidized bed reactor was performed with a bed of granular material in the form of corundum (Al<sub>2</sub>O<sub>3</sub>) The fluidizing agent was air, in which oxygen was simultaneously a carrier of atoms for diffusion. Realized research for the reduction of the number of processes and the selection of only the most targeted ones was performed based on about mathematical planning of experiences. This way of conducting research allows in a relatively short time, analyze the influence of technological parameters on the assessment of the heat and mass transport intensity in the process of oxide coating production. The completed FADT oxidation processes in the temperature range 580-640°C in 6, 8, 10, 12 hours allowed to obtain in the surface layer titanium substrates of the oxygen-saturated diffusion zone being an oxygen solid solution in titanium  $Ti_{\alpha}(O)$ , while on the porous surface  $TiO_2$ -oxide. The oxidation of titanium at elevated temperatures > 550°C results in the formation of a crystalline oxide layer. It has a zoned structure consisting of a layer adhering to a metallic substrate - TiO, intermediate -  $Ti_2O_3$  and a layer directly interacting with the environment in the form of TiO<sub>2</sub> - anatase, rutile or mixtures of these oxides [pos. 4.B2, 4.B3, 4.B5]. On the basis of carried out tests, it was found that oxygen transport in the above mentioned layers depends to a large extent on defect of the structure of the substrate, defect density and their type and is most probably caused by the dominant inward oxygen diffusion through anion vacancies [pos. 4.B4]. Therefore, the mechanism of FADT fluid bed oxidation differs from that of conventional methods. This is due to the advantages of spontaneous activation of the mechanical surface as a result of the interaction of the fluidized bed aeromechanical agent during oxidation, which is associated with continuous defectation of the surface of the substrate with simultaneous oxidation, decisive for an increased number of active centers to form oxide oxide coating during oxidation. Titanium surface is then active and has strong affinity to oxygen, which causes the mechanism of fluidized oxidation to be combined with simultaneous oxygen dissolution in the metallic phase and porous formation (result of surface activation) of the oxide layer. It can also be noticed that particularly intensely saturated with oxygen areas of the substrate are intergranular borders with increased energy and changeable state of stress, as a result of activation with  $Al_2O_3$ particles. Performing surface treatment of titanium using a fluidized bed, it allowed to obtain compact porous oxide layers. Based on them, the thickness variations were determined depending on the oxidation process parameters used. The thicknesses of the obtained oxide layers were also

determined based on the results of oxygen concentration distribution profiles after the oxidation process, and the obtained results correlated well with the results obtained on the basis of observations of fractures with SEM method. On the basis of the obtained distribution profiles of elements in the surface layer of oxidized Grade 2 titanium, the oxygen diffusion depth was estimated depending on the oxidation process time used, which was approx. 9 - 15 µm. In addition, a change in the intensity of concentrations in the transition zone, characterized by a mild decrease in oxygen concentration as the distance from the sample surface is observed, will determine the change of the diffusion mechanism type from the vacancy mechanism to inward oxygen diffusion through macrodefects (open pores, grain boundaries, layers interface), which also affects the state of stresses in the oxide coating. [pos. 4.B6, 4.B13, 4.B15]. Such surface preparation results in significant increase of surface development, increase of surface activity, increase of surface adsorption and allows to increase mechanical anchoring of oxides formed through short-term fluidized bed oxidation with low impact factor of aeromechanical material granular on the surface in the stream of flowing gas, which is the carrier of oxygen for the production of coatings, deposition of the oxide coating produced by the surface method.

The titanium substrates prepared in the FADT process were then subjected to the processes of hybrid oxidation treatment with surface methods. The methodology for hybrid oxidation was carried out in three stages. The first stage concerned the implementation of titanium substrate technology in the broadly understood hybrid oxidation processes, i.e. the combination of the indicated FADT fluidized bed process successively with the formation of thin oxide coatings on the surfaces of substrates using surface methods: PVD - magnetron sputtering, LST - laser texturing and Steam-Ox - induction method in steam environment. At this stage, as a result of physicochemical tests of the surface and adhesion tests and the inteface of the so-called anchoring thin oxide layers to substrates after FADT, the most-preferred hybrid processes were selected, which were verified in the aspect of improving the properties of substrate functionality, including mainly bioactivity. Hybrid processes FADT + PVD magnetron sputtering were implemented for the following parameters: I process: pressure 3 Pa, atmosphere 90% Ar / 10% O<sub>2</sub>, power 300 W, target Ti, sample-target distance 60 mm; II process: pressure 3 Pa, atmosphere 100% Ar, power 350W, target TiO<sub>2</sub>, sample-target distance 60 mm. In turn, the FADT + LST process was carried out using Nd: YAG laser radiation with a wavelength  $\lambda$  = 1064 nm, power 50W, where the energy and pulse time were respectively 0.90x106 W / cm2 and 155 ns [pos. 4.B1, 4.B3, 4.B4]. Another method of hybrid oxidation treatment was the method of induction steam oxidation named by the authors of Steam-Ox, which is the subject of the patent PL No. 221053 pt. The method of modifying the surface layer of implants from titanium alloys (Sposób modyfikowania warstwy wierzchniej implantów ze stopów tytanu) [pos. no. 4.B17]. The process of titanium surface oxidation in steam is carried out with induction method, as a result of the action of variable magnetic field and the induction of eddy currents around the oxidized element, in the environment of steam. The advantage of the method is to bring heat mainly to the surface of the element, reducing the heat impact on the core while maintaining the required strength properties and

improving the corrosion resistance. The element is initially heated in the environment of steam obtained as a result of evaporation of water after heating it from the surface of the element and then cooled to room temperature without air access. As a result of the catalytic interaction of the surface of the metal material with the steam, the activity and oxidation potential of the Me + H<sub>2</sub>O system increases. The oxidation process takes place in the system of connected vessels, as a result of which the water vapor pressure during the process is regulated by the height of the water column in the system - the supply tank - a sealed working chamber. Initially, the element is immersed in water, which in contact with the heated surface undergoes evaporation and the generated steam fills the working chamber, and thus sets the working pressure. As a result of this process, the element is in an environment of steam. The indicated hybrid combination of coatings in turn provides a synergistic increase of properties important from the point of view of the bioactivity of the implant-tissue system, including limitations of the residual stress gradient between the diffusion fluidity saturation zone Ti with oxygen, and a tight and homogeneous thin coating of TiO<sub>2</sub>, while reducing surface roughness and improving its morphology. The combination of methods in the said hybrid system allows for a synergistic improvement of surface effects affecting the intensity of subsequent deposition of hydroxyapatite coatings, which will be proved later in the description of scientific achievement. The use of surface methods provides a tight oxide coating with a favorable morphology for the nucleation of hydroxyapatite-based compounds.

The second stage of the research concerned the determination of the characteristics of the oxide layers produced on substrates after individual hybrid processes. Determining the material characteristics of oxides consisted of microstructure and quantification studies and qualitative phase contribution of oxides (rutile, anatase) forming the stratified structure of substrates and their influence on the surface condition, i.e. topography, state of stresses, thickness, homogeneity, etc. In order to verify the assumptions of the scientific purpose of accomplishing and carrying out the research, the following methods were performed after oxidation, including:

- stereometric tests to assess the impact of surface activation and diffusion treatment on grain size change in the core and in the surface zone before and after the FADT oxidation processes, [pos. 4.B6, 4.B9, 4.B13],
- surface morphology studies using atomic force microscopy AFM Veeco Instruments MultiMode AFM microscope), in order to compare the influence of the type of activation process on surface properties before and after oxidation in a fluidized bed and after treatment with hybrid methods [pos. 4.B1, 4.B9, 4.B10, 4.B14],
- metallographic structural studies using light microscopy LM Axiovert metallographic Carl Zeiss microscopy) and scanning electron microscopy (SEM - JEOL JSM-6610LV scanning electron microscope), to assess the effects of structural changes corresponding to individual oxidation technologies, evaluation of the zonal structure of the surface layer and its chemical composition (SEM-EDX) as well as the comparison of saturation effects of the titanium surface layer with oxygen after FADT [pos. 4.B1, 4.B2, 4.B6],

- studies using transmission electron microscopy TEM, STEM, EFTEM Microscope S / TEM Titan 80-300 by FEI, to assess the effects of hybrid oxidation (FADT + PVD), the construction of the oxidized layer both in the surface zone and in the transition zone (interface) (TiO<sub>2</sub> PVD coating / TiO2 coating FADT) [pos. 4.B3],
- studies on the chemical composition of coatings using secondary ion mass spectroscopy (SIMS - IMS 6F CAMECA spectrometer) and optical emission spectroscopy in glow discharge (GDOES - HJY-JY GD-PROFILER 2 spectrometer), to assess the depth of oxygen diffusion in the surface zones [pos. 4.B3, 4.B11, 4.B12, 4.B13, 4.B15, 4.B16],
- phase analysis using X-ray methods, GID-XRD, μ-XRD X-ray diffractometer Seifert 3003TT and Empyrean PANalytical; in order to evaluate the phase composition of the oxide coatings obtained [pos. 4.B1, 4.B3, 4.B5, 4.B8, 4.B11, 4.B13],
- phase analysis by Raman spectroscopy (RS Horriba Yvon Jobin LabRAM HR spectrometer) and surface analysis studies using CLSM laser confocal scanning microscopy, to determine the type and contribution of oxide phases in the TiO<sub>2</sub> coating mixture on the surface [pos. 4.B1, 4.B2, 4.B3, 4.B5, 4.B8],
- microhardness testing using the Knoop method microhardness tester FUTURE-TECH FM-7, surface layer of titanium bases after FADT in order to evaluate the distribution of microhardness and mechanical properties of the oxidized surface layer [pos. 4.B6, 4.B7, 4.B15],
- stress testing in the surface layer using the sin<sup>2</sup>Ψ method Seifert 3003TT X-ray diffractometer, to verify the effect of the hybrid oxidation process type on the state of stress in the surface layer of titanium Grade 2 [pos. 4.B3, 4.B4],
- testing of wear resistance of oxide coating using the Scratch-Test method and Kulotest, in order to evaluate the improvement of tribological properties of titanium elements and samples after oxidation [pos. 4.B7, 4.B9, 4.B10, 4.B11, 4.B16],
- testing of mechanical properties of coatings after hybrid oxidation treatment using the nanoindentation method - nanoindenter Micro Materials Ltd. NanoTest Ventage [pos. 4.B3]
- tests of electrochemical corrosion resistance using the potentiodynamic method (AMEL 7050 potentiostat together with the three-electrode system and Juniorassist software) [pos. 4. B13],
- testing of corrosion resistance in the environment simulating human body fluids (SBF – Kokubo test), to determine the effect of oxidation conditions on the corrosion properties of oxide coatings and verification of the biocompatibility of titanium elements by determining the occurrence of growth zones of hydroxyapatite compounds [pos. 4.B1, 4.B3, 4.B4],
- studies on the orientation of crystallographic planes by the method of diffraction of backscattered electrons (EBSD - SEM HITACHI SU70 microscope with Thermo Scientific analysis systems), in order to determine maps of easy diffusion routes (phase grain borders

and interfaces) of oxygen and the influence of the arrangement of crystallographic planes on the effects of saturation Grade 2 with titanium [pos. 4. B3],

 studies on the kinetics of oxide coating formation, in order to optimize the oxidation parameters and determine the mechanism model based on the interface layer theory, oxygen balance and evaluation of the fluidized bed aeromechanical agent, intensification of ion spraying in the hybrid method and evaluation of diffusion phenomena [pos. 4. B1, 4.B6, 4.B7, 4.B11, 4.B14, 4.B16]

Obtained information about properties and mechanisms of oxidation and morphology of creation of zoned structure of the surface layer and oxide coatings, served to comprehensively compare the effects of titanium oxidation with various hybrid methods and determine the impact of a given process on the structure and physical, chemical and mechanical properties of the obtained  $TiO_2$  thin oxide coatings. The results of the oxidation of Grade 2 titanium substrates using the hybrid method indicate differences in the oxygen concentration distribution profile (SIMS) in the surface layer after individual oxidation methods. In the PVD method, one can notice a thin zone of occurrence of the oxide coating  $TiO_2$  and the previously formed solution zone  $Ti_{\alpha}(O)$ , which is the result of diffusion impregnation of the titanium bases in a fluidized bed in the FADT process. The consequence of this is the obtaining in the oxidized zone of areas with a constant concentration of oxygen - the zone of TiO<sub>2</sub> oxide PVD (about 1.0 µm) and areas with variable decrease of oxygen concentration with the increase of the distance from the surface (about 1.5-2.0  $\mu$ m) - zone of porous TiO<sub>2</sub> FADT oxide and Ti<sub>a</sub>(O) diffusion zone with a thickness between 9-15 µm. The observations above confirmed the results of maps of the distribution of oxygen concentration with the contrast of elements in titanium substrates after hybrid oxidation performed by transmission electron microscopy with TEM-EFTEM Energy Filtered Transmission Electron Spectroscopy of Microscopy [pos. 4.B3, 4.B4]. The tests carried out in the diffusion zone, interface zone and PVD zone confirm the occurrence of a TiO<sub>2</sub> porous oxide coating after fluidized bed FADT resulting from the interaction of oxygen with the aeromechanically activated surface of the substrate and a tight coating of TiO<sub>2</sub> PVD oxides embedded and anchored in the diffusion zone TiO<sub>2</sub> FADT. The STEM method tests performed clearly show the transition zone (interface) produced after hybrid oxidation (FADT + PVD). The thickness of the FADT-PVD interface was about 600-800 nm. In this zone, the areas of nano-pores with irregular shapes and with different sizes are visible in the range from 20 to 60 nm. The distribution of pores in the zone and their size are well shown by the maps of oxygen concentration in titanium substrates also made by the TEM-EFTEM method. They also indicate that the areas with the presence of nanopores are places for easy anchoring of particles deposited by PVD TiO<sub>2</sub>. From the obtained results, one can also notice a clear zone of PVD TiO<sub>2</sub> build-up over the transition zone as a result of achieving a critical amount of particles in the process of chemisorption for further formation of the zone in the adsorption process on the surface of the porous TiO<sub>2</sub> after FADT. TEM-EFTEM studies also show the deposition of oxide layers as a result of combining TiO<sub>2</sub> PVD nanoparticles (40 nm+60 nm) with a rutile variant with FADT TiO<sub>2</sub> particles. Interesting results were also provided by studies on the influence of orientation

of crystallographic planes on oxygen transport using backscatter electron diffraction (SEM / EBSD - Electron backscatter diffraction) [pos. 4.B3]. The analysis of EBSD map results shows that there is a different orientation of the crystallographic surfaces of the oxide phases at the surface and in the  $Ti_{\alpha}(O)$ , diffusion zone, where the correlation with the occurrence of the planes with crystallographic orientation (1010) is visible. However, at the surface there are also areas with crystallographic orientation (2110). It follows that the facilitated nucleation of oxide phases of  $TiO_2$  in the diffusion zone takes place in grains with orientation (1010), which is caused by a change in the speed of diffusion streams for this orientation due to the incomplete casting of octahedral gaps. As a consequence, slower delivery of oxygen atoms (smaller diffusion flux) to grains with this orientation will lead to rapid saturation of the Ti Grade 2 surface, and this in turn may lead to slower nucleation of the TiO<sub>2</sub> oxide phases. This indicates the formation of a transition zone – interface as a result of the hybrid oxidation applied, as confirmed by the TEM tests carried out above. In addition, analysis of the TiO<sub>2</sub> layer at a thickness of 1  $\mu$ m showed a strong texture of the planes towards [200] direction.

Equally attractive results regarding the phase composition of Ti Grade 2 after hybrid oxidation were provided by XRD X-ray phase analysis results ( $\mu$ -XRD, GID) [pos. 4.B4, 4.B5]. The  $\mu$ -XRD diffractograms for the Ti diffusion zone after fluidized bed oxidation (FADT 640°C, 8 h) showed the presence of TiO and TiO<sub>2</sub> peaks in the rutile variety. Peaks from Ti<sub>a</sub> are also visible, which is related to changes in the structure of the titanium lattice by oxygen in the interstitial areas and confirms the formation of the Ti<sub>a</sub>/Ti<sub>a</sub>(O) diffusion layer during oxidation. On the other hand, GID-XRD diffractotograms obtained for titanium after hybrid treatment (mainly PVD) showed the presence of the strongest peaks coming mainly from the TiO<sub>2</sub> phase of the FADT phase produced by TiO<sub>2</sub>, but peaks from TiO<sub>2</sub> in the rutile variety are also visible, suggesting the presence of anatase mixed structure and rutile after hybrid oxidation by PVD method, LST method and Steam-Ox.

The oxide phases on the surface of titanium substrates after hybrid treatment were additionally analyzed using Raman spectroscopy [pos. 4.B5, 4.B6, 4.B8]. Literature data indicate that for the TiO<sub>2</sub> coating in the rutile variant, the bands in the range of wavelengths: 143 cm<sup>-1</sup> (B1g), 236 cm<sup>-1</sup> (broad band), 447 cm<sup>-1</sup> (Eg), 612 cm<sup>-1</sup> are active. (A1g), and 826 cm<sup>-1</sup> (B2g) and six active bands for the anatase phase, i.e. 144 cm<sup>-1</sup> (Eg), 197 cm<sup>-1</sup> (Eg), 399 cm<sup>-1</sup> (B1g), 513 cm<sup>-1</sup> (A1g), 519 cm<sup>-1</sup> (B1g) and 639 cm<sup>-1</sup> (Eg) [21]. In addition, it was observed that the intensity of anatase-specific bands decreases with the increase in the oxidation temperature, which confirms the reduction in the proportion of metastable anatase in the produced TiO<sub>2</sub>, and its gradual transformation into TiO<sub>2</sub> rutile. The remaining characteristic bands in the range of wave numbers: 604-609 cm<sup>-1</sup>, 416-445 cm<sup>-1</sup> and 231-243 cm<sup>-1</sup> are derived from the oxide phase of TiO<sub>2</sub> in the rutile variety, which is the dominant phase in oxidized Ti Grade 2 samples by FADT. In addition, it was observed that the bands are shifted towards the lower values of the wave numbers, which suggests the occurrence of compressive stresses in the coatings thus confirming their phase differentiation. Analyzing the Raman spectra for samples subjected to a hybrid oxidation using the FADT+PVD method, the occurrence of peaks was observed, mainly in the range of wave numbers: 143 cm<sup>-1</sup>, 198 cm<sup>-1</sup>, 395 cm<sup>-1</sup>, 515 cm<sup>-1</sup> 634 cm<sup>-1</sup>

characteristic for anatase. In the case of the FADT+LST hybrid treatment, peaks are visible in the range of wave numbers characteristic of rutile:  $612 \text{ cm}^{-1} \text{ cm}$ ,  $412 \text{ cm}^{-1}$  and  $237 \text{ cm}^{-1}$ . It is the dominant phase in these substrates, but the share of anatase is also evidenced by the peak in the range of wave numbers at 145 cm<sup>-1</sup>. The applied hybrid treatments made it possible to obtain different oxide structures, important from the point of view of the use in biomedicine. Numerous works prove that only TiO<sub>2</sub>, in the rutile variant, is the active phase for the growth of hydroxyapatite, but the results obtained in scientific achievement indicate that the favorable state of the surface for the improvement of bioactivity is a mixture of stable TiO<sub>2</sub> in a variant of rutile with metastable TiO<sub>2</sub> in anatase variety obtained in hybrid processes, which will be confirmed by bioactivity studies. [22-25 / pos. 4. B8].

In order to analyze and assess the state of stress of the substrate and the oxide coatings formed, stress tests were carried out using the sin2 $\Psi$  method for reflexes (101), at a diffraction angle of 2 $\Theta$  = 46.99, radiation deflection in the surface zone with a thickness of approx. 3.0 µm. The measurement was done using the Seifert 3003TT device in Bragg-Brentano and GIXRD geometries using KaCo radiation = 0.17902 nm. Reflections were recorded for 3 symmetrical rotation angles in the range of 0-150. The analysis of diffractograms was carried out using Rayflex software and PDF4 + 2013. Stresses in the border zone were estimated at approx. -970 MPa. The stresses were estimated using the Rayflex / Analyze software for elasticity constants E = 112 GPa and n = 0.33. The position of the reflections is based on the maximum of reflections (Parabola Fit). The results showed a favorable stress change at the FADT substrate - TiO2 PVD oxide coating, which indicates the advantage of implementing hybrid oxidation processes in the aspect of improving the energetic state of the surface of titanium substrates, which in turn is very important in biomedical applications [pos. 4.B4].

The surface quality of the implant has a significant impact on the reactions occurring at the implant-biosystem interface. Surface modification (functionalization) through the production of layers or coatings affects the intensification of osseointegration processes, tissue regeneration as well as the behavior of the implant during operation. The topography and chemical composition of the substrate surface is of the greatest importance for the creation of a permanent connection between the implant and the bone tissue [26-29]. In order to increase the biocompatibility with the human body and bioactivity, the titanium substrates have been subjected to surface modification by hybrid oxidation to obtain the appropriate topography of the surface and its energetic state, in order to obtain control of hydroxyapatite based growth and tissue regeneration. It is known that titanium is considered a biocompatible material, however, for particles below 10 µm, including layers, inflammation has been observed in in vitro and in vivo tests, which indicates their cytotoxicity, and is very detrimental to the biofunctionality of titanium implants. Analyzing, therefore, the purposeful literature data seems to develop hybrid methods in surface engineering allowing for obtaining thin oxide coatings with a permanent connection with a properly prepared substrate. Roughness has a significant impact on the biological response of pure titanium implants. Osteoblasts are more likely to adhere to the rough surface of titanium, whereas fibroblasts and epithelial cells are mainly formed on the smooth

surfaces of titanium implants. The rough surface is more preferred in osseintegration processes due to better bone growth on the implant surface, and thus greater adhesion to the implant. The average surface roughness and properties depend, however to a large extent from the applied surface treatment, which is a key aspect of improving the properties of implants [30]. It is worth mentioning that most literature data show that the surface roughness parameter should be close to approx. 0.8-1µm to improve the rate of osseintegration at the substrate-tissue interface [31]. Observations and studies of titanium substrates after hybrid oxidation indicate significant differences in surface morphology, compared to the conventional oxidation effects, e.g. only with PVD. The results of AFM atomic force microscopy studies indicate that the result of the hybrid method is to obtain a very favorable surface morphology, which indicates a synergistic interaction of physicochemical phenomena on the surface during the oxidation of FADT + PVD / LST / Steam-Ox. This is related to the oxygen transport facilitated as a result of fluidized treatment to the continuously defected Ti support and the formation of a porous diffusion zone in titanium, which consequently facilitates the subsequent adhesion of TiO<sub>2</sub> particles in non-equilibrium surface methods (PVD, LST, Steam-Ox). The confirmation of the above statement is the formation of dispersive TiO<sub>2</sub> oxide particles in the diffusion zone, which have been shown to study the distribution of oxygen concentration in the surface layer using GDOS and SIMS. Analysis of the obtained results indicates that the penetration depth of oxygen is about 1.5+2.5 µm, except that in the near surface zone a much higher concentration of oxygen is visible. It follows that the mechanical activation zone of the deposit corresponds to the distance at which the oxygen concentration is greater than 35 atomic percent oxygen (according to with the Ti-O phase equilibrium system) [pos. 4.B3, 4.B5]. Research and analysis of substrates after initial hybrid oxidation indicates significant differences in surface morphology. This is related to the effects of various oxidation processes, initially carried out in a fluidized bed (mechanical activation) and the interaction of porous oxide TiO<sub>2</sub> FADT, with thin layers of oxides formed by PVD and LST method, which significantly improves the surface morphology of titanium substrates. The formation of a thin oxide layer in the LST laser texturing method depends mainly on the parameters of the laser beam (beam power, pulse length, texturing speed), which creates oxide micro-textures on the surface with a depth of approx. 2+3 µm. However, the microstructure of substrates after FADT + LST treatment also revealed cracks in the treated areas from the point of view of biomedical applications, it should be avoided due to the increased state of stress and, as a result, the mechanical strength of the substrates and the ability to release the effects of degradation to the body, resulting in inflammation of the tissue [32]. The surface roughness parameter after fluid bed oxidation was  $R_a = 1.38 \mu m$  and after hybrid oxidation was respectively  $R_a = 0.741$  and  $R_a = 0.977$  µm for the PVD and LST method and  $R_a = 0.832$  for the Steam-Ox method. The analysis suggests that as a result of the hybrid method, a favorable surface morphology is obtained, which indicates a synergistic effect of the physicochemical reaction on the surface of substrates after hybrid oxidation [item no. 4.B1, 4.B3].

The third stage of research in the scientific achievement was the determination of the biofunctionality of substrates as a result of the bioactivity tests of the surface. Obtained layers different in terms of chemical structure and micro and nanotopography were evaluated from the point of view of bioactive properties, in contact with artificial physiological fluids c-SBF2 in the so-called Kokubo test. It is well known that there are two types of bioactivity, osteoprotective bioactivity and osteoconductive bioactivity, depending on the speed and mechanisms of interaction of implant tissues [33-36]. To optimize biochemical activity and biomechanical compatibility of titanium substrates, the authors focused on the functionalization of hybrid titanium substrates both by creating titanium bioactive layers on substrates, as well as modifications of the composition and physicochemical properties of thin oxide layers (mixture TiO<sub>2</sub> rutile + anatase). The mechanism of adhesion of the implant to the tissue is directly related to the tissue response at the implant interface. Each material implanted into living tissues is not indifferent and causes a certain tactile response. When the bioactive material is implanted, a number of biophysical reactions take place on the implant-tissue surface and biochemicals. It is also known that the bioactive material is one that provides a specific biological response at the boundary of the material, which results in the formation of a bond between the tissues and the medium in an environment compatible with osteogenesis. For various bioactive materials, the binding mechanism (time dependence), binding strength, and thickness of the binding interface are different [37-40]. However, the rate of development of interfacial bonding at the substrate-tissue interface in SBF etc. can be defined as the level of bioactivity. The relative bioactivity and time dependence of interfacial formation and the level of bioactivity of a particular material is therefore related to the time of formation of more than 50% of the tissue - substrate interface [41-43]. In the studies carried out, titanium substrates after hybrid treatment were tested in terms of their bioactive properties by immersion in c-SBF2 (Kokubo tests) for 7, 14 and 21 days and results were analysed with the SEM-EDX method. Research on the surface of titanium substrates after hybrid oxidation (especially FADT + PVD) confirmed very intensive incubation and subsequent deposition of dispersive, globular compounds based on hydroxyapatite (HAp), (basis for accelerated osseintegration processes), initially forming particularly intense at the limits and in areas of defective coating and then as a result of stabilization of surface energy of HAp particles, very intensively on the surface of substrates [pos. 4.B1, 4.B3, 4.B4]. HAp particles form agglomerates and clusters, which indicates the wide usage of formed titanium substrates in biomedical applications. It can be concluded that hybrid oxidation of titanium includes new methods of combining phenomena of oxygen transport in oxide layers, in the area of shaping beneficial changes of titanium surface properties for biomedical applications. Intensified particle growth based on hydroxyapatite compounds and their clusters indicate the possibility of applying the above-mentioned techniques in the processes of bone and soft tissue growth and regeneration.

#### SUMMATION

The methodology of completed research has enabled the achievement of the goals of scientific achievement in three stages. The first stage concerned the technology of producing titanium substrates in the broadly understood hybrid oxidation processes, i.e. combining the above-mentioned fluidized bed oxidation processes FADT successively to form thin oxide coatings on the surfaces of substrates using PVD, LST methods and Steam-Ox methods. At this stage, as a result of physicochemical tests of the surface, adhesion tests of the thin oxide layers of substrates were selected the most beneficial hybrid processes, which were verified in the aspect of improving the properties of biofunctional substrates, mainly bioactivity.

The second stage of the conducted research concerned the development of characteristics of oxide layers produced on substrates after particular hybrid processes. Determination of material characteristics of oxides consisted in microstructure research and determination of quantitative and qualitative phase proportions of oxides (rutile, anatase) forming on the structure of substrates and their impact on surface condition, i.e. morphology, state of stresses, thickness, homogeneity, etc.

The third stage of the research, consisted in determining the biofunctionality of substrates as a result of bioactivity tests of the surface. Obtained layers differentiated in terms of chemical structure and micro and nanotopography were evaluated from the point of view of bioactive properties in contact with artificial body fluids c-SBF2 in the Kokubo test. The results of these tests were verified on the basis of layer adhesiveness studies as well as studies related to the obtained topography and surface physicochemistry.

In conclusion, it must be stated that increasing the bioactivity of materials is always a challenge for biomedical engineering and surface engineering. To improve the properties of titanium for biomedical applications, hybrid oxidation methods were used and a favorable system was obtained: Ti<sub>a</sub> core / Ti<sub>a</sub>(O) solid solution - diffusion top layer / TiO<sub>2</sub> thin oxide coating (preferably a mixture of rutile and anatase). Such a system is one of the ways to protect the surface of titanium substrates while ensuring biofunctional properties (bioactivity) to increase the intensity of the interaction of compounds with properties supporting tissue regeneration e.g. hydroxyapatite. As a result of the performed tests, a change in the oxygen concentration profile was obtained to form a diffusion zone of a solid oxygen solution in titanium  $Ti_{\alpha}(O)$  and a porous  $TiO_2$  titanium oxide coating in the rutile variety with a favorable substrate-coating stress state, which constitutes a homogeneous and strengh "foundation" for further modification in surface processes (PVD, LST, Steam-Ox etc.). The mentioned oxidation methods (FADT + PVD / LST / Steam-Ox) in a hybrid system allowed to use the advantages of spontaneous mechanical activation of the surface as a result of interaction of the fluidized bed aeromechanical medium, which is associated with continuous defectation of the surface of the substrate with its simultaneous oxidation. In turn, when the number of active centers increases, it decides about the subsequent transport of oxygen mass during the formation of a thin TiO<sub>2</sub> oxide

coating. The hybrid combination of coatings created in this way ensures a synergistic increase of properties important from the point of view of biocompatibility of the implant-tissue system. These properties are mainly the limitation of the stress gradient between the diffusion fluidity saturation zone Ti with oxygen, and a tight and homogeneous PVD coating, with simultaneous improvement of its morphology. The combination of methods in the said hybrid system allows for the substrate to be functionalised by improving the kinetics of surface phenomena and effects, affecting the intensified bioactivity of substrates, confirmed by the increased intensity of deposition of hydroxyapatite compounds in the Kokubo test. Oxide coatings obtained by the mentioned methods are characterized by low thickness and very good adhesion, which depends on many factors, including, inter alia, the preparation of the surface of titanium substrates for hybrid processes. The hybrid oxidation of titanium therefore includes new ways of combining phenomena of oxygen transport in oxide layers, in the field of shaping beneficial changes of titanium surface properties for biomedical applications. The increased growth of hydroxyapatite particles and aggregates indicates the possibility of applying the above-mentioned techniques in the processes of bone tissue growth, which will be an inspiration for further evaluation of the reasons for the accelerated increase in HAp particle deposition using the technologies implemented.

#### CONCLUSIONS

- 1. Modification of Ti Grade 2 substrates by fluidized bed oxidation results in the formation of a diffusion zone enriched with  $Ti_{\alpha}(O)$  oxygen characterized by a favorable state of stress and a substrate for subsequent hybrid processes used to produce thin oxide coatings mixture of TiO<sub>2</sub> rutile and anatase.
- 2. The attractiveness of Ti Grade 2 substrates produced by the fluid atmspheric diffusion treatment FADT is related to the continuous defect of the surface layer during saturation of titanium with oxygen, as a result of interaction of the aeromechanical medium of the deposit with the atmosphere. This allows for controlled defect of the surface zone during oxidation, and thus the production and increase of the number of active centers, easy diffusion paths, as well as the formation of a micro / nano-porous structure of TiO<sub>2</sub> rutile.
- 3. The FADT method, as a result of the surface activation directly in the saturation process with oxygen transport in Ti Grade, creates a  $Ti_{\alpha}(O)$  diffusion zone with a favorable state of compressive stresses, providing a substrate for subsequent intensive deposition of  $TiO_2$  oxide coating in rutile and anatase. This allows the defect of the surface zone during oxidation, thus producing and increasing the number of active centers, and paths for easier diffusion of oxygen.
- 4. The use of the FADT + PVD hybrid treatment allows for the production of a homogeneous, tight and a continuous oxide coating with a mixture of TiO<sub>2</sub> phases of rutile and anatase on the surface Ti Grade 2. This is related to the adhesion of PVD coatings to the FADT substrate

(TEM results) and the occurrence of surface sorption processes (chemisorption, adsorption, desorption). This state of phenomena and the effects of oxidation of titanium using the hybrid method are primarily determined by the parameters of production of individual oxide zones and their synergistic interaction in the hybrid way of combining them.

- 5. The combination of methods of oxidation of titanium substrates in the hybrid method improves the surface roughness of substrates, which is particularly useful in the aspect of the easier and more intensified process of deposition of hydroxyapatite compounds in a globular form.
- 6. The presented method of deposition of oxide coatings with the hybrid method is a new solution for biomedical applications showing the directions of biocompatible layers production in biomedical applications.

#### APPLICATIONAL ASPECT OF THE RESULTS AND RESEARCH PERSPECTIVES

The widely understood goal of achieving scientific achievement is to reduce the frequent occurrence in implant-tissue systems of metallosis phenomena, and improvement of functional properties of the surface of titanium substrates, in particular bioactivity. The realized multivariant processes of hybrid oxidation of the surface of titanium substrates allowed to improve the properties of biofunctional titanium substrates. The presented achievement concerns the essence and significant area of ensuring the comfort of life of people whose organisms were subject, among other things, to diseases of the bone system. This state of affairs causes limited motor skills and reduced efficiency of people in the production period, reduced physical fitness and pain of people above all at retirement age. The results obtained during the research inspired the author to undertake comprehensive research on the oxidation of titanium-based materials. Conducting hybrid oxidation research allows to compare the obtained oxidation effects with various methods used in scientific and industrial centers, and to broaden knowledge not only about kinetics, course of phenomena during the process of hybrid oxidation, to obtain the best possible properties for specific biomedical applications, but also to develop mechanisms for oxidation to obtain repeatability of processes. The research conducted by the author initially included FADT processes of fluid and atmospheric titanium diffusion treatment, however, understanding the mechanisms and kinetics of oxidation allowed to initiate the idea of combining physical, chemical and utility properties of substrates in after various oxidation processes. Obtained information on kinetics and mechanisms of oxidation and morphology of creation of zoned structure of oxide coatings and the surface layer, served to develop innovative hybrid technologies for the implementation of modern titanium substrates (VI generation implants) for biomedical engineering applications to improve the quality of life. The implementation of the research allowed for a comprehensive assessment of the comparison of hybrid titanium oxidation effects on its structure and physical, chemical and mechanical properties. In turn, the use of surface methods allowed to significantly reduce the time of oxidation technology and significantly improve the adhesive properties of oxide coatings. Obtained results of hybrid processes were presented at international and

on scientific conferences as well as seminars with the participation of industry. The proposed solution for the hybrid treatment of titanium oxidation points to new possibilities of modifying and shaping the properties of oxide layers, in the aspect of biomedical applications. Intensification of the growth of particles and hydroxyapatite clusters indicates the possibility of applying the above techniques in the processes of bone tissue growth in bone implantology and dentistry.

The presented method of depositing oxide coatings with the hybrid method is a new solution for biomedical applications, consistent with new trends in biomaterials and surface engineering combining various material engineering techniques to improve implants and medical devices. The completed research has allowed the development of new technological solutions in the field of hybrid oxidation of implants, and obtaining original data on the properties of prepared materials regarding the influence of surface physicochemistry and micro and nanotopography on the nature of biological response, mainly the effect of bioactivity on speed and the type of osseointegration will allow to broaden the knowledge about the bioactivity phenomenon.

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# 5. Description of other scientific and research achievements

# 5.1. Work experience – general information

I was born on June 25<sup>th</sup>, 1985 in Czestochowa. After finishing Romuald Traugutt II High School in Czestochowa, in 2004 I took up master's studies at the Faculty of Materials Science and Ceramics, AGH University of Science and Technology in Cracow. In 2009, I graduated with a very good result, obtaining a master's degree in the field of Materials Engineering with the specialization of Protection against corrosion. During 3<sup>rd</sup> to 5<sup>th</sup> year of my studies I obtained a scientific scholarship. From 2005, I was a member of the international student organization IAESTE - International Association for the Exchange of Students for Technical Experience, which runs a program of exchanging students of technical experience. As IAESTE member, I was the chairman of the internships promotion section, as well as the supervisor of foreing students from Turkey, Norway, Spain and Germany realizing internships at the AGH University of Science and Technology in Cracow. During my studies, for two years I was also the chairman of the Residents' Council of the Faculty Student House and I took an active part in the work of the Faculty Council of Student Self-Government, among others in the organization of the annual Ceramics Ball. I was also a member of the AZS volleyball section B at AGH. In 2009, after obtaining a master's degree in material engineering, I began doctoral studies at the Faculty of Production Engineering and Materials Technology at the Czestochowa University of Technology. As a PhD student, I was a triple holder of Czestochowa University of Technology Rector scholarship for the Best Third Degree Students, as well as in the years 2013-2014 holder of the scholarship project DoktoRIS for the innovative Silesia Voivodship EU programme. Doctoral dissertation entitled Phenomena and effects of active screen influence on ion nitriding processes, which I defended in 2014, obtaining the scientific degree of doctor of technical sciences in the field of Materials Engineering. Currently from March 2015, due to the creation of Engineering Logistics specialization, I am employed as an assistant professor at the Institute of Logistics and International Management at the Faculty of Management at the Czestochowa University of Technology. At the same time, with the agreement of the Czestochowa University of Technology Rector, from June 3<sup>rd</sup> to September 30<sup>th</sup> 2015, as part of a project carried out in cooperation with the industry, I was employed as a coordinator of the Research and Development R&D Department at the company Narzędziownia Bogdan Pszenica in Praszka. In 2016, I became a scholarship holder of the prestigious competition "Scholarship for Outstanding Young Scientists" implemented under the auspices of the Minister of Science and Higher Education. Currently I am the supervisor of the Local Student Organization Committee of the IAESTE at the Czestochowa University of Technology. I am also a Chairman of the Commission for Innovation and Invention at FSNT – NOT in Częstochowa and a Member of the Board of the The Wire Association International Poland Chapter.

#### 5.2. Scientific and research activity

I started my research activities as part of my master's thesis Three-dimensional interdiffusion, at the Faculty of Materials Science and Ceramics of the AGH University of Science and Technology in Cracow, which concerned the analysis of the interdiffusion phenomena in aluminum alloys AA6061, as well as in elements the so-called diffusion couples and diffusion multiples in the aspect of diffusion modeling in three-dimensional geometry, for the applications of new Cu-Ag-Ni-Sn alloys for lead-free solders in the processes of diffusion bonding materials for the electronics industry and aerospace. I carried out the research under the supervision of professor Marek Danielewski in cooperation with employees of the Delft University in the Netherlands and the EMPA Institute of Swiss Federal Laboratories for Materials Science and Technology in Switzerland. The test results were used to assess the effect of changes in chemical composition in particular areas in multidiffusion interfaces on the properties of alloys, related to the change of their viscosity and wettability during light alloys diffusion bonding processes. I presented the results of research conducted in the master's thesis as part of the presentation entitled 3D Geometry Interdiffusion, which was awarded at the International Master's Thesis Competition within GENIUS EUROPA '2009 in Budapest.

After obtaining a master's degree in engineering, I started doctoral studies at the Faculty of Production Engineering and Materials Technology at the Czestochowa University of Technology at the Institute of Materials Engineerng. The subject of my scientific research in this period concerned the issues of heat and mass transport (nitrogen and oxygen atoms in plasma nitriding, controlled gas nitriding, fluidized bed oxidation) in metallic materials surface layer during diffusive processes, including iron based alloys (Fe armco, austenitic steels, tool steels) and titanium based alloys (Ti Grade 2, Ti Grade 5). The research carried out consisted of using the innovative active screen ion nitriding method to assess the kinetics of diffusion phenomena and nitriding process mechanisms to improve the saturation efficiency of the surface layer, with the reduction of the occurrence of unfavorable zones in the nitrided layer. The essence of the research also concerned the comparison of the kinetics of nitriding processes, including the NITREG controlled gas nitriding process commonly used in industrial conditions, with active screen plasma nitriding processes. Inspiration for the implementation of scientific research and searching for advantages of active screen plasma nitriding method were research carried out in international scientific centers and industrial units connected with shortening long-term processes while lowering the temperature and modifying the phase composition of nitrided layers.

The proposed criteria for assessing the effects of nitriding lead to a reduction in the consumption of gas and energy media, as well as increasing the service life of nitrided elements, used in the aerospace, automotive industry, as well as in biomedicine. The result of the scientific research was the development of model and mechanism of heat and mass transport in the active screen nitriding processes. A significant reduction in the temperature of the processes, together with the determination of the driving force of nucleation at the nanoscale, while nitriding at low temperature also allowed to optimize processes for specific operational applications, including gas sensors, magnetic materials and biomaterials. The

research problem which corresponds to the present trends in surface engineering, related to the repeatability of processes and properties of thermally processed products has been also solved. Realization of scientific research as part of the doctoral thesis allowed for:

- analysis of the nitrided substrate properties in order to evaluation of the phase system energy interaction, including the effect of mechanical and physicochemical activation of structural components, on the nucleation driving force in the micro and nano scale, both in the process of gas and active screen plasma nitriding,
- comparison of microstrucutre morphology and properties of nitrided layers obtained by active screen plasma nitriding and gas methods, to select nitriding parameters (temperature, time, atmosphere composition etc.),
- comparison of the kinetics of cathode plasma nitriding with active screen plasma nitriding, in order to determine the effect of active screen on phenomena and effects occurring during the metallic materials saturation process,
- development of a model of active screen nitriding mechanism based on iron and titanium substrates.

The proper selection of nitriding methods related to the implementation of scientific research was to determine the reduction of the defects in the nitrided layer, related to a rapid change in nitrogen concentration in the diffusion layer and at the nitrided layer / substrate core interface, reduction in the thickness of the nitride zone and  $\gamma'$  nitrides, and the limitation of porous and brittle  $\epsilon/\epsilon+\gamma'$  zone. In turn, the selection of a wide temperature range in the research enabled the acquisition of information on the relationship and changes in the constitution of the surface layer of alloys for:

- determining the effect of active screen application, on the surface layer saturation with nitrogen, and on the kinetics of nitrided layer growth and its structural and strength properties,
- determination of the effect and role of carbon atoms in Fe armco on the diffusion nitrogen permeation processes, during ion nitriding with the active screen method and the occurrence of the uphill diffusion effect,
- determining the effects of surface activation during the heating and subsequent diffusion saturation of Fe armco, in the aspect of grain refinement, as a result of the recrystallization of the substrate and defect of the subsurface zone, decisive for the heat transfer and the number of easy diffusion paths and internal stresses in the nitrocarbon layer of Fe armco,
- determination of the diffusion kinetics depending on the process temperature and cooling after the nitriding process and its influence on the participation of particular phases  $\epsilon / \epsilon + \gamma'$ and  $\gamma'$  in the process of nitrided layers forming with a mild nitrogen concentration profile.

An especially important stage of the conducted research was the development of the model of the ion nitriding mechanism with the application of an active screen, based on the effects of heat and mass transport and the structure change of the nitrided substrate (Fe alloys, Ti alloys) with the surface significantly activated under the active screen. An important aspect in the development of the ion nitriding mechanism model was the analysis of ion-nitrided layers by means of backscattered electron diffraction (SEM-EBSD). It was performed to determine maps of nitrogen easy diffusion paths (phase and interfacial grain boundaries) and the influence of crystallographic planes on saturation effects.

Additional investigation of the carbon concentration profile from the surface (in Fe alloys) revealed the occurrence of the phenomenon of splintering / climbing the diffusion of carbon called uphill diffusion, which involves the migration of C atoms under the solution zone  $\varepsilon + \gamma'$  or  $\varepsilon/\varepsilon + \gamma'$ . Local change in the carbon concentration under the solution zone leads to the formation of a concentration gradient and changes in the thermodynamic activity of the carbon, in the presence of increasing nitrogen concentration in the zone, which in consequence is the driving force for its diffusion in iron based alloys.

Obtained results of the described research allowed me to present my doctoral dissertation entitled *Phenomena and effects of active screen influence on ion nitriding processes*, which I defended on October 17<sup>th</sup> 2014, obtaining the scientific degree of doctor of technical sciences in the Material Engineering scientific discipline. The Supervisor of my doctoral thesis was Associate Professor Tadeusz Frączek. The results of the research were used both to design subsequent plasma nitriding technologies, as well as to model the mechanism and morphology of plasma layers formation. The confirmation of the above statement is considerable interest in proposed solutions in plasma nitriding by industrial units and international scientific units, which is confiremed by co-authored awards, diplomas and prizes received at international inventions and innovations exhibitions in Brussels, Zagreb and Bucharest, [Annex No. 4 item. II. D1-D7]:

- T. Frączek, J.Jasiński, M. Olejnik, <u>J.J. Jasiński</u>, 16.09.2009, Unconventional technology of ion nitriding of austenitic stainless steels, 7<sup>th</sup> International Fair of Inventions New Ideas, Products and Technologies Zagreb 2009 – Silver medal, Croatia 2009
- T. Frączek, J.Jasiński, M. Olejnik, <u>J.J. Jasiński</u>, 28.10.2009, Unconventional glow discharge nitriding technology of high-chromium steels, The 13<sup>th</sup> edition of The International Trade Show for Inventions and New Technologies Inventica Bucarest – Gold medal, Romania 2009
- T. Frączek, J.Jasiński, M. Olejnik, <u>J.J. Jasiński</u>, 19.11.2009, Short-term and low-temperature glow discharge nitriding technology of high-chromium steels, The Belgian and Interntional Trade Fair for Technological and Innovtion Brussels – Gold medal, Brussels, Belgium2009
- T. Frączek, J.Jasiński, M. Olejnik, <u>J.J. Jasiński</u>, 7.12.2009, Short-term and low-temperature glow discharge nitriding technology of stainless steels, Seoul International Invention Fair SIIF 2009 – silver prize for commending excellent and creative effort to invention, South Korea, 2009
- T. Frączek, M. Olejnik, <u>J.J. Jasiński</u>, 22.10.2010, High-chromium steels economical glow discharge nitriding technology – Wystawa wynalazków International Warsaw Invention Show IWIS 2010, Złoty medal, Poland 2010

Simultaneously carried out in the field of scientific research during doctoral studies at the Institute of Materials Science at the Częstochowa University of Technology, there were studies on the oxidation of titanium substrates using the fluidized bed diffusion saturation method FADT, followed by hybrid methods that were aimed at modifying the surface layer of titanium substrates and the surface functionalization of the above-mentioned titanium substrates. The conducted research on the oxidation of titanium substrates is the basis of my scientific achievement titled *Functionalization of titanium substrates to improve bioactivity in biomedical applications,* required in accordance with from art. 16 sec. 2 of the Act of 14 March 2003 on academic degrees and academic title, and on degrees and title in the field of art (Journal of Laws of 2017, item 1789).

Detailed discussion on the scientific achievement purpose and obtained results I presented in point 4 a-c, Annex No. 3. After PhD, from March 1<sup>st</sup> 2015 I continued research

on the issues indicated in scientific achievement as an assistant professor at the Institute of Logistics and International Management, Faculty of Management, Częstochowa University of Technology, which was associated with the creation of a new course of the studies – Engineering Logistics. My scientific activity at the Institute of Logistics and International Management is mainly focused on material engineering discipline and surface engineering, including research on the scientific achievement related to the issues of hybrid oxide coatings, with special functional properties formed in oxidation processes.

Realization of the research issues included in the scientific achievement has allowed for the development and implementation of biofunctional titanium substrates in hybrid oxidation processes, which is a combination of diffusion saturation processes FADT (fluid atmospheric diffusive treatment) with surface methods used to form thin TiO<sub>2</sub> coatings. The variable oxides obtained during the research (mixture of TiO<sub>2</sub> rutile and TiO<sub>2</sub> anatase) on the surface of titanium substrates allowed, in the bioactivity studies, to determine changes in the rate of hydroxyapatite compounds growth, thus optimizing substrates for selected biomedical applications, mainly in bone tissue implants and dentistry. The essence of the conducted scientific research was also the analysis of the phenomena of the interaction of selected heating solutions used in the process of hybrid oxidation of titanium, after the previous surface activation with various methods, including both mechanical and mechanical-chemical. The tests were also carried out to analyze the titanium oxidation processes by fluid diffusion treatment (FADT) and the hybrid method (FADT + surface methods: I: PVD magnetron sputtering, II: induction steam oxidation method – Steam-Ox / according to patent PL No. 221053, III: laser surface texturing method – LST).

A particularly important issue in the studies I carried out concerned the study of phenomena and effects of the generated inteface of the Ti99.2 substrate / TiO<sub>2</sub> oxide on the adhesion of oxide coatings and their physicochemical properties, followed by biofunctional properties, mainly bioactivity. The implementation of the substrate / oxide interface study allowed to determine the impact of the state of the interfacial zone on the mechanical, chemical and surface properties (topography, structure) of oxide coatings and determining the mechanism of oxide coatings formation and the surface layer of substrates after a given hybrid process to determine the most favorable composition of layers in terms of bioactivity. Analysis of the results of scientific research also concerned the development of diffusion process kinetics of the titanium saturation with oxygen, including phase transitions, occurring during individual processes for variable parameters etc.

The thicknesses of the obtained oxide coatings and the depth of oxygen diffusion after the process of titanium fluidized bed oxidation were determined based on the results of the oxygen concentration profile using the GDEOS and SIMS methods. As expected, the oxide coating and the depth of the oxygen diffusion layer raise as the temperature and time of the oxidation process increase. I have also shown that the change in concentration intensity in the transition zone is characterized by a gentle reduction of oxygen concentration relative to the distance from the substrate, which in the case of FADT process determines the change of the diffusion mechanism and has a beneficial effect on the change of stress in the oxide coating and diffusion zone, which measurements I performed with the  $\sin^2\Psi$  method which results clearly confirmed the existence of favorable compressive stresses in oxide coatings. Subsequently, the subtrates after FADT oxidation were subjected to hybrid processes using PVD magnetron sputtering, Steam-Ox induction steam oxidation method and the LST laser surface texturing method. As part of the research, plasma oxy-nitriding process was also carried out using the innovative active screen method.

The zone structure and properties of the obtained oxide coatings and the transition zone of hybrid coatings were evaluated on the basis of research on oxidized samples fractures, using SEM electron microscopy with composition analysis in micro-areas SEM-EDX and using transmission electron microscopy TEM and STEM method, as well as X-ray phase analysis GID-XRD and µ-XRD and Raman spectroscopy, which showed that on the surface of hybrid media quasi-equilibrium mixture of titanium oxides rutile and anatase was formed. Mechanical tests of coatings were made using the nanoindentation method. In order to present the effects of titanium diffusion saturation of with oxygen and the difference in crystallographic orientation of the oxide phases tested, I also performed the SEM-EBSD electron backscatter diffraction research. As part of the research I also evaluated the corrosion resistance of the oxide coatings obtained, in conditions simulating human body environment SBF (Simulated Body Fluid), and analyzed them based on SEM images and chemical analysis in micro-areas SEM-EDX, where I confirmed intensive growth of biocompatible HAp hydroxyapatite compounds, which indicates favorable conditions for the production of coatings with favourable, more precisely the required biocompatibility in implantology.

The implementation of scientific research allowed me to comprehensively evaluate the comparison of the effects of titanium oxidation with various hybrid methods and to determine the impact of applying a given oxidation method on the structure, physical and chemical properties and mechanical thin oxide films obtained. In turn, the use of surface oxidation methods allowed to significantly reduce the time of oxidation technology (induction steam oxidation, PVD hybrid oxidation) and to improve the adhesion properties of oxide coatings to substrates after FADT diffusion treatment. On the basis of the obtained test results and their analysis, it was possible to state that titanium oxidation in the fluidized bed under the aeromechanical interaction favors the formation of porous oxide coatings on the titanium substrates, beneficial from the point of view of mild changes in the state of stress and oxygen concentration in the surface layer, with the possibility of modification in PVD, Steam-Ox and LST processes and further applications in biomedicine. The results of the tests have made it possible to verify the improvement of the biofunctional properties of the substrates, as well as select functional substrates for specific implantology applications. Achieving the assumed objectives of research on the surface functionalization of titanium will be a significant extension of knowledge about the processes titanium substrates oxidation, the production of thin oxide coatings and the impact of surface type and morphology to obtain the predicted and repeatable properties of bioactive implants for applications in skeletal system diseases, including the spine and lower and upper limbs, as well as in dentistry.

The research allowed to indicate following most important conclusions:

- The method of diffusion oxidation of titanium substrates in a fluidized bed (FADT) results in the formation of a porous oxide coating TiO<sub>2</sub> and a oxygen-saturated Ti<sub>α</sub> diffusion zone (O) with a favorable stress state of the coating / diffusion zone system.
- 2. The resulting porous coating / diffusion zone is the foundation for the subsequent deposition of thin TiO<sub>2</sub> oxide coatings rutile / anatase in hybrid oxidation processes.

- 3. The attractiveness of titanium substrates produced by FADT is associated with mechanical activation and continuous defectation of the surface zone during oxidation, thus generating new active centers and increasing the number of roads for easy diffusion with the formation of a nano-porous TiO<sub>2</sub> coating on the surface of the substrate.
- 4. The use of hybrid treatment after fluidized oxidation allows the formation of a homogeneous, dense thin TiO<sub>2</sub> coating in the rutile and anatase variants on the porous TiO<sub>2</sub> FADT oxide.
- 5. The synergistic effect of hybrid oxidation processes affects to obtain a gradient state of stress and a favorable surface roughness of titanium substrates for next intensive deposition of hydroxyapatite compounds and as a consequence increasing the bioactivity of titanium substrates.
- 6. Among the hybrid methods used for the functionalization of titanium substrates, the FADT + PVD method is the most advantageous method for improving bioactivity of the titanium substrates.
- 7. The presented results of functionalization of titanium substrates using the hybrid method constitute a prospective solution for biomedical applications and may indicate new directions of biocompatible layers and substrates formation used in implantology.

I have carried out the work in the described research within 12 research projects financed by the Ministry of Science and Higher Education, the National Science Center, the Foundation for Polish Science FNP and projects financed from the European Union funds, as well as Statutory Research in the home scientific unit:

- Project No. BS / MN 604/302/2016 / P, Mass transport analysis in issues of the process of diffusion saturation of materials for the electromechanical industry, (2016-2017), Częstochowa University of Technology, Faculty of Management, faculty project for Young Scientists - project manager.
- Project No. BS / MN 604/302/2018 / P Analysis of mass transport in the issues of the process of diffusion saturation of materials for the electromechanical industry and biomedicine, (2018-2019), Częstochowa University of Technology, Faculty of Management, departmental project for Young Scientists - manager project.
- Project No. RPLU.01.02.00-06-0050 / 16-00, Carrying out research and development works in the scope of developing self-service recycling machines and intelligent waste collection system, (2016-2019), Regional Operational Program of the Lubelskie Voivodeship for 2014-2020, Research and innovation, task implementation 3 / D.1.2RPOWL / 2018 - project contractor.
- 4. Project HOMING PLUS / 2013-8 / 7 Mechanical properties of zirconium / zirconia system at high temperatures the role of internal and interfacial stress, (2014-2015), Foundation for Polish Science FNP project contractor.
- 5. Project No. NN 507231240, Activation of titanium oxidation processes for the purpose for biomedical applications, (2011-2014), NCN National Science Center project contractor.
- DoktoRIS scholarship project Scholarship program for innovative Silesia, (2013-2014), POKL 2007-2013 Activities 8.2 Transfer of knowledge, Sub-measure 8.2.2 Regional Innovation Strategies, Regional Human Resources; European Social Fund- project scholarship holder.
- 7. Project No. NN 507472837, Modification of the structure of titanium and new generation alloys in the aspect of biomedical applications, (2009-2013), National Center for Science NCN-project contractor.
- Project No. NN 507296239 Short-term and low temperature glow-discharge nitriding of nonnitriding metallic materials, (2010-2013), NCN National Science Center - project contractor.

- Project No. BS / MN-202-306 / 2011 Kinetics of Fe armor's ion nitriding with active screens (Active Screen), (2011-2012), Czestochowa University of Technology, Faculty of Production Engineering and Materials Technology, faculty project for Young Scientists - project manager.
- Project No. BW-202-201 / 2010 Modeling of thermo-chemical processes of metal plastics, (2010-2012), Częstochowa University of Technology, Faculty of Production Engineering and Materials Technology, Own Research - project contractor.
- Project No. R150352 Technologies of shaping the structures of materials for engine elements with increased durability, (2007-2011), Ministry of Science and Higher Education / Research and development projects - project contractor.
- 12. Project No. NN507445434, Unconventional methods of low temperature glow-discharge nitriding of metallic materials used in medicine, (2008-2011), NCN National Science Center project contractor.

Particularly important stage of my scientific and research activity was the coordination of the WNDRPOP.01.03.02-16-007/13 project in cooperation with R&D Department of the Narzędziownia Bogdan Pszenica company, financed by the European Union under the Regional Operational Program, Opolskie Voivodeship for 2007 -2013 Sub-measure 1.3.2, Investments in innovation in enterprises, European Regional Development Fund, in which I carried out design works and technological trials related to the launch and implementation of the spotting press to the R&D Department for spotting and covering large-size molds (about 30 tons) for pressure die casting of AI and Mg light alloys for the automotive industry, incl. for the leading manufacturer of trucks. The total value of the project was PLN 1,968,000.00. I also participated in two projects under the Human Capital Operational Programme financed from the European Union funds, including:

- 1. Priority IX Development of education and competences in regions, Operational Program Human Capital 2007-2013, European Social Fund, (2012-2013), Project UDAPOKL.09.05.00-24 792 / 11-00 pt. Renewable energy as an opportunity for development of rural areas.
- Operational Program Human Capital 2007-2013, European Social Fund ESF, Priority

   "Employment and social integration", Measure 1.1 "System support for labor market
   institutions", (2011-2013), Project No. POKL.01.01.00-00-019 / 10, Developing a set of
   national standards of professional competences required by employers the contractor of the
   project,

where within the mentioned projects I was a lecturer at seminars on Renewable Energy Sources and I developed competence procedures of national professional competences of the profession: Heat treatment furnaces operator.

The implementation of the above-mentioned projects and works allowed me to develop as a co-author a total of 68 publications published in national and international scientific journals, including 14 publications indexed in the JCR database (list A of the Ministry of Science and Higher Education). Publications according to the Web of Science database (WoS), were cited 61 times, and their total Impact Factor is 25.45. My Hirsch index according to WoS is 5. The obtained research results, which are closely related to my scientific achievement and research projects carried out, allowed me to receive as a co-author 4 national patents and development of 1 patent application. As part of the presentation of the results of the research, I delivered 7 papers at national and international conferences and scientific seminars, and I actively participated in 20 academic conferences, including 4 national and 16 international.

My scientific and research activity also included co-authorship and implementation of laboratory research stands. As important I consider the stand related to research on

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scientific achievement connected with induction steam oxidation processes using to perform tests on hybrid oxidation of titanium substrates, which was prepared as part of the patent application [Annex No. 4. item I.B.19]; as well as developing design assumptions for the induction heating device for thermal fatigue testing technologies of hot work steels in the context of their application in the aluminum alloy extrusion process and in the production of brake discs for the automotive industry [Annex No. 4 item II.B.4]; As part of my activities at the Institute of Materials Engineering at the Faculty of Production Engineering and Materials Technology, I organized a Research and Didactic Laboratory for surface and coatings engineering, in which I implemented a PVD - magnetron sputtering stand, and a device for laser surface treatment methods, with the use of which I realized pilot hybrid hybrid research processes related to scientific achievement [Annex No. 4 item II.F.2]. Currently, I am involved in the implementation of the project related to development and implementation of an innovative construction of heat exchangers walls for power units in conventional, fluidal and CHP power plants. The proposed solution consists in replacing the existing technology of construction and production of tight walls, consisting of connecting pipe-flat-tube elements by a new method, by removing the separating flat bars and applying the so-called double-sided pipes welded directly with one joint. The solution allows to reduce the number and length of welds, reduce stress and reduce the failure of energy devices and increase their efficiency, which was confirmed by the conducted stress simulation tests, in the prepared model of the heat exchanger wall in the power boiler [Annex No. 4 item. II.B.1].

The acquired research experience served in addition to the implementation of works mentioned above allowed me to conduct research commissioned by industrial units in the field of technological development of machines and constructions, quality of materials assessment and determination of machine elements and tools destruction causes. One of the the most important in my opinion, it is worth to mention these expertise works connected with development of guidelines aimed limiting and often eliminating the causes of destruction and premature wear of parts of machines and tools for the automotive, glass, foundry, processing and recycling, pharmacy industry including:

- <u>J.J. Jasiński</u>, K.Wojsyk, (2019), Opinion on the causes of damage to the anchor stirrer blades of the MZUTL-200 CCF device for CENTRUM MEDICUM POLAND MSc in pharmacy Małgorzata Karpińska-Trojanowska Łódź – manager.
- J. Nowakowska-Grunt, <u>J.J. Jasiński</u>, K. Wojsyk, K.Kudła, (2018), Project No. RPLU.01.02.00-06-0050 / 16-00, implementation of task 3 / D.1.2RPOWL / 2018 report on research work BZ-604-07 / 2018 Analysis of the solution and system validation in terms of obtaining a safety certificate for devices for purchase, sorting and preliminary processing of selected secondary raw materials, Częstochowa University of Technology, Częstochowa 2018.
- <u>3. J.J. Jasiński</u>, (2018), Assessment of foundry defects on the surface of cast iron wheels 275/119 and wheels 7741 for GUSS-EX Warsaw, Opinion of the Appraiser of the Regional Chamber of Commerce and Industry RIPH in Częstochowa - head of the work.
- 4. <u>4. J.J. Jasiński</u>, (2018), Assessment of surface contamination in cast iron wheels 275/119 and wheels 7741 for GUSS-EX Warsaw, Opinion of the Appraiser of the Regional Chamber of Commerce and Industry RIPH in Częstochowa head of the work.
- J.J. Jasiński, (2017), Verification of defects in cast iron castings after machining for GUSS-EX Warsaw, Opinion of the Appraiser of the Regional Chamber of Commerce and Industry RIPH in Częstochowa 2017 - work manager.

- 6. <u>J.J. Jasiński</u>, (2017), Verification of the defect in the KENWOOD NX-5200E radiotelephone enclosure, for PPHU MARKO company Marek Chwist, Poraj, Expert opinion of the Regional Chamber of Commerce and Industry RIPH in Częstochowa 2017 work manager.
- 7. <u>J.J. Jasiński</u>, J.Jasiński, (2016), Expertise Research and material analysis of piston rods for applications in the automotive industry for FA KROSNO S.A., Częstochowa 2016.
- 8. <u>J.J. Jasiński</u>, (2016), Metallographic evaluation of samples after cooling in a polymeric divider and hardening oil for the company ZKZ Zakład Kół Zębatych S.C. Borkowski, Olszacki Oleśnica work manager.
- 9. J.Jasiński, <u>J.J. Jasiński</u>, (2014), Metallographic examinations and analysis of the causes of shaft cracking W2040100 for Neapco Europe Sp. z o.o. Praszka work contractor.
- 10. J.Jasiński, <u>J.J. Jasiński</u>, (2013), Metallographic examinations of cracks and analysis of crack causes of the die for extrusion of aluminum alloys for the company EDP Obróbka Stali Sp. z o.o. Bytom work contractor.
- J. Jasiński, M.Lubas, <u>J.J. Jasiński</u>, (2012), Expertise Metallographic analysis of mold materials for the production of glassware for Stolzle Częstochowa Huta Szkła, Częstochowa 2012 - contractor of the work.
- 12. J. Jasiński, <u>J.J. Jasiński</u>, (2012), Expertise Analysis of rupture causes of VW360KB rivets for TRW Polska (ZF Friedrischafen AG) - contractor of the work together with the presentation of research results for foreign contractors in the analysis of rivet rupture causes in the rivet production process pt. Analysis of cracking in VW360KB tubular rivets, Częstochowa 2012.
- J. Jasiński, <u>J.J. Jasiński</u>, (2011), Expertise Metallographic analysis of the Spider 2400 cross after the DYNO test for the company Neapco Europe Sp. z o.o., Częstochowa 2011 - work contractor.
- 14. J. Jasiński, <u>J.J. Jasiński</u>, (2011), Expertise Metallographic analysis of axle shaft for an industrial plant Neapco Europe Sp. z o.o., Częstochowa 2011 work contractor.
- 15. J. Jasiński, M., Lubas, <u>J.J. Jasiński</u>, (2009), Metallographic microscopic analysis of cast iron used on molds for the production of glassware for Stolzle Częstochowa Sp. z o.o., Częstochowa 2009 expert contractor.
- 16. J. Jasiński, <u>J.J. Jasiński</u>, Expertise Metallographic analysis of 1S6W 3W008-AA cross-braces for TeDrive Poland Sp. z o.o., Częstochowa 2009 expert contractor.

An important achievement in research commissioned by industrial units is the realization of 28 opinions on innovation for the companies that applied for projects financed from European Union funds, designated to increase innovation and competitiveness of industry as a result of the implementation of modern technologies. Among the most important opinions of technological solutions that received funding and which in 2019 applied for the acquisition of EU funds, I would like to point out following:

- <u>J.J. Jasiński</u>, (2019), Opinion on innovation: Production technology of geometrically complex components of new-generation aerospace turbofan engines for the company AVIOMECHANIKA Sp. z o.o. - PCz BZ-604-06 / 2019 - work manager.
- 2. <u>J.J. Jasiński</u>, (2019), Opinion on innovation: Implementation of SOPHUS mobile systems for SOPHUS Sp. z o.o. Technical Services and Training Team NOT 2019 work manager.
- J.J. Jasiński, (2018), Opinion on innovation: Implementation of an advanced IT system controlling the production processes, deliveries and assembly of gates, blinds and mosquito nets for the company MIROLA MISZKA Sp. J. - PCz BZ-604-09 / 2018 - work manager.
- J.J. Jasiński, (2018), Opinion on innovation: Implementation and commercialization of an innovative process of comprehensive cleaning of motor vehicles, including commercial vehicles and special for PPHU FERGOPOL company - PCz BZ-604-08 / 2018 - work manager.

- J.J. Jasiński, (2018), Opinion on innovativeness: Launching services in the field of advanced machining of large-size parts, including hubs of sea wind rotors for the company USŁUGI FREZARSKO-TOKARSKIE DANIEL BULENDA - PCz BZ-604-02 / 2018 - work manager.
- J.J. Jasiński, (2017), Opinion on innovativeness: Automatic bending technology for rebar in 2D and 3D with the use of servomotors implemented in order to launch an innovative product in the form of geosynthetic anchors used in engineering construction for the company PRZEDSIĘBIORSTWO OBROTU WYROBAMI HUTNICZYMI CENTROSTAL KIELCE SA -PCz BZ-604-09 / 2017 – manager.
- J.J. Jasiński, (2017), Opinion on innovation: Technology of surface preparation of multimetals before powder painting based on innovative zirconium-chromium conversion technology for CENTRUM LAKIEROWANIA PROSZKOWEGO ECOLAK Sp. zoo. - PCz BZ-604-06 / 2017 work manager.
- J.J. Jasiński, (2017), Opinion on innovation: Implementation of innovative 3D printers for the production process of Christmas decorations for the company PPH IMPULS - PCz BZ-604-04 / 2017 - work manager.
- J.J. Jasiński, (2017), Opinion on innovation: The use of innovative elements and solutions in a modern portal automatic car wash for the company SPEED OIL SP. J. - PCz BZ-604-01 / 2017 - work manager.
- <u>J.J. Jasiński</u>, (2015), Opinion on innovation: Implementation of a UV printer for the production of glass Christmas decorations for the company PPH IMPULS - PCz BZ-604-03 / 2015 - work manager.
- J.J. Jasiński, (2015), Opinion on innovation: The solution of innovative elements min the latest vehicle washing technology KARCHER SB / MB for the company AUTOLUX Grzegorz Gicala - PCz BZ-604-01 / 2015 - work manager.
- Z. Wojtynia, <u>J.J. Jasiński</u>, (2012), Opinion on the technology: Production of arch elements of the archway of the excavation of headings from V-shaped sections (TH) with grooves for cooperation with stirrups in the link for the company ZK KOZAMEX ZPChr - Technical Services and Training Team FSNT - NOT 2012 - work contractor.

A special promotion of achievements related to scientific-research activities, mainly in the field of glow discharge nitriding with the active screen method of iron alloys and titanium alloys were the previously mentioned innovative solutions presented on international exhibitions of innovations and inventions, which were awarded with special prizes, Minister's prizes, medals and diplomas, including:

- Diploma of the Minister of Science and Higher Education for the Częstochowa University of Technology, Institute of Materials Engineering, (2011) Technology of economic ion nitriding of high-chromium steels, T. Frączek, M. Olejnik, <u>J.J. Jasiński</u>, Warsaw 2011
- Diploma of the Minister of Science and Higher Education, (2010), Technology of short-term, low-temperature ion nitriding of hard-boiling high-chromium steels, (2010), T. Frączek, J. Jasiński, M. Olejnik, <u>J.J. Jasiński</u>, Warsaw, 2010
- Award of the Minister of Education, Innovation and Development of Romania, (2009), Short term and low-temperature glow discharge nitriding technology of high-chromium steels, T. Frączek, J. Jasiński, M. Olejnik, <u>J.J. Jasiński</u>, INNOVA Brussels, Belgium 2009
- 4. Diploma of the Minister of Science and Higher Education for the Częstochowa University of Technology for the promotion of inventions at domestic and foreign exhibitions of innovations and inventions in 2011, Warsaw 2012
- 5. Diploma of the Minister of Science and Higher Education for the Częstochowa University of Technology for the promotion of inventions at domestic and foreign exhibitions of innovations and inventions in 2010, Warsaw 2011.

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My scientific activity is also related to the reviewing of projects co-financed by the NCBiR National Center for Research and Development and publications in renowned magazines from the JCR database. As an NCBiR expert, I was a reviewer of 2 projects in the INNOCHEM POIR 1 / 1.2 / 2017 / Operational Program Smart Growth program. I have also made 20 reviews of publications in the following renowned international scientific journals, including:

- 1. ASTM Materials Performance and Characterization (2 reviews)
- 2. Journal of Laser and Optics (1 review)
- 3. Archives of Metallurgy and Materials (1 review)
- 4. Hutnik Wiadomości Hutnicze (1 review)
- 5. Przemysł Chemiczny (1 review)
- 6. Advances in Materials Physics and Chemistry (1 review)
- 7. Zeitschrift für Metallkunde: International Journal of Materials and Research (1 review)
- 8. Journal of Molecular Structure (3 reviews) (Certificate: Outstanding Reviewer 01.2018)
- 9. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (1 review)
- 10. International Journal of Engineering and Technology Innovation IJETI South Korea (2 reviews)
- 11. International Conference on Advanced Technology Innovation 2017 South Korea (4 reviews)
- 12. Advances in Technology Innovation AITI South Korea (1 review)
- 13. Biuletyn Wojskowej Akademii Technicznej WAT (1 review).

During my master's and doctoral studies, as well as after doctoral thesis, I did 3.5 months international internship at Kennametal Sintec HTM in Biel / Bienne (Switzerland) in the field of powder metallurgy and hot isostatic pressing HIP technology, in which I carried out technological reports related with the determination of the tempering curves of ledeburitic steels for applications in polymer processing and procedures for preparing samples of newly-obtained powder steels for impact tests using the Charpy V method, which I presented in following studies:

- 1. J.J. Jasiński, PM Steel X255W, X260W2 tempering curves determination.
- 2. J.J. Jasiński, Reference Charpy impact test PM specimens preparation.

I also did a 3.5 month internship at E-Control Glas GmbH in Furth im Wald (Germany) in the field of technology for the production of smart materials used for the production of Smart Windows, where I carried out tasks related with the creation of an internal and external control device for performing the brightening and darkening tests of 48 smart windows, in order to optimize their work parameters and preconditioning before the final exploitation, which I presented in following studies:

- 1. J.J. Jasiński, Internal 48 Controllers Electronic Hardware.
- 2. J.J. Jasiński, External 48 Controllers Electronic Hardware.
- 3. J.J. Jasiński, VBG 120x40 transparency measurements and preconditioning optimization.

As part of my scientific and research activity at the Czestochowa University of Technology, I completed an internship at Bodycote Polska Sp. z o.o., which was realized in order to obtain the results of research for a doctoral thesis on the subject of gas and plasma nitriding processes to realized comparative analyzes of the mentioned technologies. As part of the internship I also got acquainted with technologies of heat treatment (vacuum hardening) and chemical heat treatment (controlled gas nitriding, nitrocarburizing, oxynitriding etc.) of the elements and tools for the automotive, defense and electromechanical industries and also with the methods of preparation of metallographic specimen and analysis of microstructure in the surface layer of tool steels. I also took a 10-day internship at Vacummschmelze GmbH

& Co. KG in Germany related to familiarization with the technology of producing thin amorphous films by the melt spinning method and their application in the power and electrotechnical industry, as well as metallographic preparation of thin films and strips.

As part of my research and development activity I also took part in certified trainings: in the field of technological, constructional and material solutions used in vibration damping elements implemented by KYB - certificate No. 323/2017; Application of Spectroscopic methods for material testing "Agilent Cary UMS UV-VIS / NIR spectrophotometer - Optical characterization by measuring the absolute specular reflectance / transmittance and scattering" organized by the company MS SPEKTRUM Sp. j. (2017), as well as in the "STRUERS Materialography" training in the field of sample preparation of materials used in metallography organized by the company STRUERS in Cracow (2012) and training "Quality control of materials using Barkhausen noise, X-ray diffraction and PRISM hole drilling methods", organized by PCB Service in Warsaw (2012).

In 2016, I became a laureate of the Minister of Science and Higher Education Scholarship for Outstanding Young Scientists in the 11<sup>th</sup> edition of the competition for my scientific and research activity. The equally important awards include the Silver Honorary Badge "For Merit for the Śląskie Voivodeship" awarded by the Marshal of the Silesian Voivodeship, for scientific, economic and cultural-social activities as well as contribution to the development of the Śląskie Voivodeship. In my scientific and research achievements, I also obtained a scholarship as part of a scholarship program for an innovative Śląsk DoktoRIS. During my doctoral studies I was three times holder of a scholarship of the Częstochowa University of Technology Rector for the Best Doctoral Students for academic performance.

Acquired knowledge and experience in both the field of scientific research and solving research problems for industry have served me to a large extent to carry out didactic activities that I presented in the next section of the application.

# 5.3. Didactic activity

My didactic activity during the doctoral studies consisted mainly on conducting exercises and laboratories for students of Materials Engineering course at the Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology in the following subjects:

- 1. Heat and Surface Treatment; seminar 15h
- 2. Heat and Surface Treatment: laboratory 30h.
- 3. Heat and Surface Treatment; seminar 30h, (assistant).
- 4. Materials Science; laboratory 15h.
- 5. Materials Science and Engineering; laboratory 15h.
- 6. Materials for the Special Applications; seminar 30h, (assistant).

After obtaining the doctor of technical sciences degree, as part of employment at the Institute of Logistics and International Management, I have conducting lectures, laboratory and seminars exercises in the following subjects:

1. Introduction to Technique, lecture 30h in the field of: Engineering Logistics.

- 2. Introduction to Technique, lecture 30h major: Bachelor's Logistics.
- 3. Fundamentals of engineering and technical design, lecture 15h + seminar 60h, major: Management and Production Engineering.
- 4. Fundamentals of engineering technical design, lecture 15h + seminar 60h, the field of Occupational Health and Safety
- 5. Research and development R&D in technology, lecture 15h, field of study: Quality and Production Engineering.
- 6. Process safety, lecture 15h, the direction of Occupational Health and Safety
- 7. Contemporary technologies for automation of logistics objects, lecture 15h + exercises in the field of: Bachelor's Logistics.
- 8. Safety of machines and devices, lecture 15h + classes 15h, direction: Occupational Health and Safety
- 9. Planning and controlling in logistics,
- 10. Financing of transport euro-projects, seminar 15h course: Logistics bachelor.
- 11. Outsourcing services in logistics, seminar 30h, major: Logistics bachelor.
- 12. E-logistics, seminar 10h, major: Logistics bachelor part-time studies.
- 13. E-logistics, lecture 15h, major: Logistics bachelor full-time studies.
- 14. Simulation in logistics, laboratory 30h, major: Logistics and bachelor's.
- 15. Computer systems in logistics, laboratory 30h, major: Engineering Logistics.
- 16. Environmental management systems, lecture 15h + classes 15h, field: Quality and Production Management (lecture in English).

As part of subjects teaching contribution, I prepared and updated didactic programs syllabuses from selected subjects, including: Fundamentals of engineering and technical design, Introduction to technique, Simulations in logistics, Computer systems in logistics and Environmental management systems. I also have a certificate entitling me to conduct classes in the E-learning system.

I was a supervisor of 7 master's theses and 27 engineering theses in the field of Engineering Logistics and Occupational Health and Safety. Currently, I am the supervisor of 11 engineer theses in the field of Logistics. I also took reviews up to 25 engineering diploma theses and up to 9 master's theses.

I consider co-organizing the didactic laboratory of surface and coatings engineering at the Faculty of Production Engineering and Materials Technology, which consisted in the organization and preparation of didactic stands for FADT fluid heat treatment technology, stands for the PVD technology - magnetron sputtering and stands for laser surface treatment, which were financed as part of research projects.

An important achievement in the field of popularization of science is my annual (from 2016) participation in the main committee and competition commission from 4th to 7th National Contest of Entrepreneurship and Management OPiZ for high school students, as well as coordinating 2<sup>nd</sup> level of competition for the Mazovia Region OPiZ Contest at the Leon Koźmiński Academy in Warsaw in 2018 and 2019.

Equally important in my didactic achievement in the field of popularizing science and related to the promotion of Logistics Engineering at the Czestochowa University of Technology is the participation in the Science and Technology Picnic "Explorer" carried out by the School No. 2 in Piotrków Trybunalski, in which I organized for the upper secondary students demonstration stands in the field of Materials Science and Transport Engineering Engineering Logistics course.

For an additional, extremely important form of education of young staff, I consider the organization of study visits to the plants of Barre Thomas Poland Sp. z o.o. (present Cooper Standard Poland Sp. z o.o.), TRW Automotive (present ZF Friedrichshafen) and Neapco Europe Sp. z o.o. implemented as part of practical classes for students 2<sup>nd</sup> year of Management and Production Engineering and 3<sup>rd</sup> year students of Materials Science, which were aimed at presenting materials and tools used in the technology of production and assembly of drive systems, safety systems and sealing systems in the automotive industry. This form of implementation of classes in industrial units not only facilitates the acquisition of issues by students in the field of material engineering related to the knowledge of materials and technologies used in industry, but also logistics and quality of materials and prefabricates ordered for production. The trips are an inspiration to seek continuous innovation and engineering solutions by students and that is why I consider it a special contribution to the didactic development of young people.

Since 2015, I have been the coordinator of the Local Committee of an international student organization conducting a vocational training program for IAESTE technical students (The International Association for the Exchange of Students for Technical Experience) at the Czestochowa University of Technology, under which students of the Częstochowa University of Technology also participated in study trips and foreign student internships. I also act as the Faculty Student Internships Coordinator at the Faculty of Management, in which I coordinate the Internship Bank unit by which I am gaining the offers of internships, apprenticeships and work for students and graduates of the Faculty of Management at the Częstochowa University of Technology.

# 5.4. Organizational activity

In addition to scientific and research activities and didactic, I am also involved in organizational activities, both at the Częstochowa University of Technology and at national and foreign organizations, scientific-technical and socio-cultural associations. During the doctoral studies I was a treasurer and member of the organizing committee of the 8<sup>th</sup> International Scientific Conference "Surface Engineering INPO'2011" in Wisła-Jawornik. As part of the conference and the preparation of conference materials in the period of 05.2011-09.2011 I also took part in the Editorial Committee of the journal Engineering of Materials (Inżynieria Materiałowa) - SIGMA-NOT Publishers. I was also a member of the organizing committee of the National Scientific Conference as part of the World Day of Health and Safety at Work at the Faculty of Management in 2014. My organizational activity at the Częstochowa University of Technology after obtaining the doctoral degree is associated with the work in the Department Anti-plagiarism unit at the Faculty of Management (in 2015-2019) and in the Team for Cooperation with the Industry appointed at the Institute of Logistics and International Management (from 2017), where I am a member responsible for coordinating cooperation with industrial units and the implementation of commissioned research for industry. As part of the organizational activity related to the organization of the conference, I was also the secretary of the International Scientific Conference "Chemical Safety and Health Protection BCHOZ '2018" organized at the Faculty of Management of AGH in Cracow.

#### Jarosław Jan Jasiński, Attachment no. 3

Currently I am vice-chairman of the Organizing Committee of the International Scientific Conference "Environmental Security and Health Protection 2019", which will be held on 3<sup>rd</sup> July 2019, as part of the 70<sup>th</sup> anniversary of the Częstochowa University of Technology.

My organizational activity does not only concern the activity at the home university, but also includes activities within scientific, technical and socio-cultural organizations and associations. Since 2017, I have been a member of the Board of the Wire Association International WAI USA Poland Chapter. As part of the Association's activity in 2018, I was the chairman of the Organizing Committee of the X Seminar of the Wire Association International WAI USA in Poland. Currently, I am the chairman of the Organizing Committee of the International Drawing Conference '2019 organized by the WAI USA Poland Chapter Association in cooperation with the Institute of Ferrous Metallurgy in Gliwice, which will be held in November 2019. As part of participation in international organizations and research networks, since 2016 I am also a member of the International Network of Heat Treatment Experts called Global Heat Treatment Network, bringing together industry and science experts, to solve problems in the field of heat and chemical-heat treatment technologies in various industry sectors. As part of my membership in the research network, I received a certified Heat Treatment Excellence 2017 training in the field of heat and chemical-heat treatment.

From among the organizational activities in national associations, I exchange my membership in the Polish Society of Materials Science PTM from 2016, Association of Engineers and Technicians of the Steel Industry SITPH from 2015, the Association, Association of Polish Engineers and Technicians SIMP from 2015, as well as in the Association of Polish Inventors and Rationalizers SPWiR since 2010. Currently, I am the Chairman of the FSNT-NOT Committee for Innovation and Invention in Częstochowa. In 2017, I was also elected to the Scientific Council of the Częstochowa Branch of the Scientific Society of Organization and Management TNOiK. From 2016 I am also a member of the Social and Cultural Association Community of Guade Mater in Częstochowa, which implements projects, competitions and exhibitions related to with poetry, art and music for the promotion of young artists and musicians.

As part of organizational activities, I also carry out work related to reviewing the projects which is connected with the function as an expert of the National Center for Research and Development NCBiR under POIR 2014-2020 sub-programme 1.1.1 "Fast Track" in the area of scientific and technological as well as economic and business criteria (from 2017). I work also as an experts from the Regional Unit of Commerce and Industry RIPH in Częstochowa in the scope of materials engineering, surface engineering, heat and chemical heat treatment, protection against corrosion, metal science and welding – Expert no. 01/06/15 from 2015. I am also a member of the FSNT-NOT Technical Services and Training Team in Częstochowa in the field of material engineering and surface engineering as well as heat treatment technologies.

My organizational activity also consists in cooperation with scientific and industrial units. As part of the research and technological meetings being carried out, I cooperate, among others with the following scientific units: AGH University of Science and Technology in Cracow, National Center for Nuclear Research in Warsaw, Institute of Ferrous Metallurgy in Gliwice, Military University of Technology in Warsaw, Institute of Precision Mechanics in Warsaw and industrial units as Neapco Europe Sp. z o.o., Zakłady Metalowe Kozamex, Kärcher Center, Narzędziownia Bogdan Pszenica, Fergopol, ZF Friedrichshafen (formerly TRW automotive), Metal Union Sp. z o.o., FA Krosno S.A., Protective Equipment Company Maskpol S.A. PGZ. I also have the rights of the Internal Auditor of the Integrated Quality Management System according to ISO 9000: 2015 / Environmental Management according to ISO 14000 / Safety and Health at Work ISO 18000 OHSAS 18001.

As an employee of the Częstochowa University of Technology in 2012 and 2018 for organizational activity, I received 2 team awards from the Rector of the Częstochowa University of Technology for organizing the International Scientific Conference INPO '2011 and organizing the OPiZ Competition in 2017.

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#### Criterion Lp. number Scientific publications in journals from the Journal Citation Reports 1. 14 (JCR). Original design, constructional and technological achievements 2. 6 realized Patents granted: a) international 3. a) ---b) national b) 4 Inventions and utility and industrial designs that have been 4. 7 exhibited at international or national exhibitions or fairs Monographs, scientific publications in magazines other than those 5. 54 in the JCR database Collective studies, catalogs of collections, documentation of 6. 14 research works, more important expert opinions Total impact factor according to the Journal Citation Reports (JCR) 7. SUM IF = 25,45 list, according to the year of publication: 77 in total; Number of publications cited according to the Web of Science 8. without database (WoS): self-citations 61 Hirsch index according to the Web of Science database (WoS) H-index = 59. Managing research projects: 10.A a) the international a) ---b) national b) 3 Participation in research projects: 10. B a) international a) ---b) national b) 12 11. International and national awards for scientific activity 9 Presenting papers on thematic conferences 12. a) international a) 5 b) national b) 2 Participation in European programs and other international and 13. 2 national programs Active participation in scientific conferences: a) international 14. 16 b) national 4 Participation in the organizational committees of scientific conferences: 15. a) 3 a) international b) 2 b) national Received awards and distinctions other than those mentioned 16. 3 above 1 17. Participation in consortia and research networks Project management carried out in cooperation with: a) scientists from other Polish centers, a) ----18. b) scientists from foreign centers. b) --c) entrepreneurs, other than those mentioned above c) 1 Participation in editorial committees and scientific councils of 1 19. magazines

### SUMMARY OF SCIENTIFIC AND DIDACTIC AND ORGANIZATION ACTIVITES

		isinski, Attachment no.
20.A	Membership in international organizations and scientific societies a) total b) including by choice	1
20.B	Membership in national organizations and scientific societies a) total b) including by choice	7 4
21.	Didactic achievements and in the field of popularizing science	4
22.	Scientific care for students	promoter of 34 thesis MSc (7) and Eng. (27) currently promoter of 11 Eng thesis
23.	Scientific care for PhD students in the capacity of: a) a tutor b) the auxiliary promoter	a) b)
24.	Internships in academic or academic centers a) foreign b) national	a) 3 b) 1
25.	Expertises or other studies made to external order	44
26.	Participation in expert and competition teams	7
27.	Reviewing projects: a) international b) national	a) 2 b)
28.	Reviewing publications in magazines: a) international b) national	a) 16 b)  4
29.	Other achievements: a) Cooperation with industrial units b) Cooperation with scientific units c) Certificates	a) 15 b) 14 c) 7

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