

ZnO COATINGS ON Ti6Al4V SUBSTRATE: STRUCTURAL AND ANTIBACTERIAL PROPERTIES IN LITERATURE REVIEW AND RESEARCH

Leonid SUKHODUB, Luidmila SUKHODUB, Mariia KUMEDA
Summy State University

Anton PANDA, Petr BARON
Technical University of Kosice

Abstract:

ZnO, ZnO/Alginate coatings were obtained on the pre-anodized Ti6Al4V substrates by the thermal substrate deposition method (TSD). In the frame of this work, the TSD method was at first applied for obtaining ZnO coating from aqueous alginate-containing and alginate-free solutions on a metal surface. XRD, SEM analyses show that the biopolymer has a significant influence on the formation of the coating, their morphology, texture, structure of ZnO nanoparticles. The average rate of ZnO deposition from alginate containing solution is 30 $\mu\text{m}/\text{min}$, while from alginate-free solutions – 6 $\mu\text{m}/\text{min}$. In the presence of alginate, spherical particles with flower-shaped inclusions are formed, while from the polymer-free solution, single crystals in the form of tetrahedral were obtained. Zone of inhibition test against Gram-positive *S. aureus* ATCC 25923 and Gram-negative *E. coli* ATCC 25922 proves the antibacterial activity of the ZnO/Alg coatings.

Key words: *thermal substrate deposition, zinc oxide, alginate, coating, antimicrobial activity*

INTRODUCTION

Metal materials, mainly titanium and its alloys, are widely used in medicine as implants for replacing solid bone tissue. However, due to the absence or poor bioactivity and osteoconductivity, there is a high probability of rejections; postoperative inflammatory processes and the slow integration of metallic implants into surrounding tissues take place (M. Epple, "Biomaterials and biomineralization," Wind, p. 165, 2007). Moreover, the aggressive conditions of the body fluids contribute to the biological corrosion of the metal implants. The surface modification of metal implants is one of the promising methods for improving the physicochemical and biological properties of these materials. It is known that bone mineral contains some substitution like sodium (Na), zinc (Zn), magnesium (Mg), iron (Fe), and carbonate (CO_3^{2-}) ions, which influence the dissolution rate of HA, control its crystallinity, lattice structure [8].

HA is flexible and can include different ions in its structure. As well it is known that microbial resistance to antibiotics has been reaching a critical level during the last decades. Given the serious health hazards of bacteria, many inorganic materials have been applied as antibacterial agents to kill bacteria. Among them, there are two-dimensional nanomaterials MoS₂ [10], graphene oxide [31], black

phosphorus [29], carbon nitride [17] as well as Ag-based materials [12]. Zinc (Zn) is essential in the human body due to its role in many biological functions. Zn^{2+} ions and zinc oxide (ZnO) particles are promising candidates to solve this problem since they possess more excellent durability, lower toxicity, and higher stability and selectivity [21]. Zn possesses antibacterial properties and is a microelement essential for cell proliferation and remodeling of the extracellular matrix [20]. Zn^{2+} is also capable of stimulating epithelial formation during wound healing. ZnO enhances cell viability and osteogenic ability [36], so it is thoroughly investigated as a potential novel antibacterial agent [18].

LITERATURE REVIEW

To date, some different strategies proposed for obtaining those surfaces that are both bioactive and antimicrobial [27]. These strategies are based on different technologies for obtaining both thin ($< 1 \mu\text{m}$) and thick ($> 1 \mu\text{m}$) antibacterial, bioactive and biocompatible coatings on various metal surfaces. Of particular note are the technology of electrophoretic deposition [15], micro-arc oxidation [35], plasma electrolytic oxidation (PEO) [23, 24], electrodeposition [4], sol-gel technology using as a bioactive compo-

ment of calcium orthophosphate, in particular hydroxyapatite, and as an antibacterial component – metal ions Zn, Ag, Se or antibiotics [27]. Also, laser cladding was used for composite Ag-ZnO-HA coatings on Ti6Al4V implants with high antibacterial activity (96.5% and 85.8% against *E. coli* and *S. aureus*). Synergistic antimicrobial activity (Ag⁺ and oxygen atom radicals) was investigated in vivo by irradiation of composite GO/Ag/Collagen coatings for 20 min with visible light, 660 nm (96.3% and 99.4% against *E. coli* and *S. aureus*, respectively). Bacterial biofilms on bone implants can be destroyed using a coating of red phosphorus (red-phosphorus-IR780-arginine-glycine-aspartic acid-cysteine), which is irradiated with infrared (880 nm) light. The biomedical activity of the Ti surfaces can be improved by pre-treatment, namely the formation of nanotube TiO₂ 3-D film with subsequent deposition of calcium orthophosphates.

ZnO nanostructures are characterized by the ability to bind the biomolecules in the desired orientation and high biological activity, resulting in enhanced sensing characteristics, that make them a suitable candidate for future small integrated biosensor devices [1].

There are main synthesis methods for oxide metal nanoparticles obtaining: solution-based [9], vapor state [30], and a biological method [6]. Template/surface-mediated synthesis is based on the fabrication of the coating on the substrate surface or the desired nanomaterial within the pores or channels of the nanoporous template [26]. There are methods for coating by ZnO described in the literature: metal-organic chemical vapor deposition and thermal evaporation, the wet chemical method [22], pulsed laser deposition, spray pyrolysis, epitaxial electrodeposition, radiofrequency magnetron sputtering. It was shown that Zn addition to HA does not modify the morphology of the hydroxyapatite coatings, developed by solution precursor plasma spraying using different zinc ion concentrations. But zinc concentration greater than 10 mol% inhibits the formation of HA and favors the formation of calcium zinc phosphate [5]. The ability to modulate the activity of osteoblasts and the antibacterial properties of zinc ions have been revealed in HA + Zn coatings applied by plasma spraying of a solution, which provides ion doping and leads to the deposition of lamellas. The resulting coatings were not cytotoxic to human osteoblasts [26]. Ti-Doped ZnO Nanoparticles Prepared by Modified Oxalate Route exhibits ferromagnetism [19]. In the presence of HA at pH 5 of about 80%, ZnO NPs undergo transformation to scholzite within 4 h. Under neutral or basic conditions, a slow transformation of about 60% ZnO NPs to amorphous inner-sphere Zn adsorption complexes within 30 days occurs. May affect the behavior, fate, and toxic effects of ZnO NPs in the environment. So, HA may affect the behavior, fate, and toxic effects of ZnO NPs in the environment [16] Addition of ZnO nanoparticles improves mechanical properties and compressive resistance of hydroxyapatite composites [11]. Incorporated into the HA, the Zn²⁺ improves biocompatibility and corrosion resistance of the coatings, fabricated on pure titanium by the electrolytic deposition [7]. Chemically bonded ceramic coatings have

been shown to exhibit exceptional corrosion resistance. Besides, zinc oxide coating has a lower reaction rate and corrosion current density than zinc oxide-free coatings [2].

The choice of synthesis method determines the physicochemical characteristics of the metal oxide nanoparticle, in particular ZnO, such as the size, dispersity, type of intrinsic and/or characteristic defects, morphology, and crystal structure. In turn, the above-mentioned factors influence on antimicrobial activity of zinc oxide. Thus, it was found that crystallographic orientation and type of surface plane of single-crystal 1-D ZnO nanowire arrays influence the antibacterial properties: the membrane with randomly oriented ZnO nanoarrays exhibited significantly superior antibacterial property. The different morphologies and crystal growth habits affect the antibacterial activity. ZnO nanostructures in the shape of rods and wires can penetrate cell walls of bacteria more easily than spherical ones. Whereas, flower-shaped ZnO nanoparticles have revealed higher biocidal activity against *S. aureus* and *E. coli*, than the spherical and rod-shaped nanostructures.

Among the various technologies, the thermal substrate deposition (TSD) technique, introduced by Kuroda [13, 14] and developed by our group [32, 33], was previously used only for the calcium phosphate deposition on titanium substrates.

In our previous work, a thin upper ZnO layer was applied to a calcium phosphate coating [25]. In presenting our work for the first time, the TSD method was used for the deposition of a biologically active ZnO coating on the anodized titanium (Ti6Al4V) substrate surface. The coating structural phases, morphological and antibacterial properties, the influence of the polymer on the formation of ZnO coatings were investigated.

THE EXPERIMENTAL PART

The following compounds were used for synthesis: zinc nitrate Zn(NO₃)₂·6H₂O, hydrous ammonia NH₄OH, sulfuric acid H₂SO₄, sodium fluoride NaF, sodium alginate (Alg) (E 401, low viscosity) manufactured by Shanghai Chemical Company Ltd, China. All components were analytically pure and used without further purification.

Two types of coatings were studied and compared in this work, namely the coating of pure ZnO and ZnO obtained in the presence of a polymer – alginate. The coatings were applied to titanium plates pre-anodized in a solution of sulfuric acid and sodium fluoride. Detailed information on the preliminary preparation of substrates and methods of deposition of coatings is given in our work [23].

The ZnO coating medium was prepared as follows: to 200 ml of 0.2 M aqueous solution of Zn(NO₃)₂·6H₂O was added drop by drop under vigorous agitation 30 ml of 25% w/w ammonia to obtain the transparent alkaline solution, containing ZnO nanoparticles. To obtain ZnO/Alg coating medium, an alkaline 3% solution of alginate was added to the above-described ZnO coating medium in a ratio of 1:50, respectively. The titanium plate immersed in the

mother ZnO or ZnO/Alg solutions were heated to a temperature of 90°C by passing an alternating electric current. The precipitation took place within 20 minutes. The coating is based on the dependence of ZnO solubility on temperature.

Instrumental methods. The X-ray diffraction studies of the sample crystallographic structure were performed on the automatized diffractometer DRON3 (LTD «Burevestnik,» www.bourestnik.ru). The surface morphology of the samples was examined using a scanning electron microscope (FEI Inspect S50).

Antibacterial activity of ZnO/Alg coatings. The modified disc diffusion method was used to evaluate the antibacterial activity of the ZnO/Alg coating. The method includes a placing the sample on an inoculated with Gram-negative bacteria *E. coli* (ATCC 25922) and Gram-positive *S. aureus* (ATCC 25923) bacteria agar plates, followed by incubation for 24 hours at 37°C. The microbial inoculum was prepared in a meat-peptone nutrient (MPN) (Makhachkala, Russia), which was used as a growing medium. The microorganisms were cultivated at 37°C and left overnight (late exponential stage of growth). Bacterial concentration corresponded to 0,5 units of optical density according to McFarland scale was achieved using Densi-La-Meter (PLIVA-Lachema, Czech Republic, wavelength 540 nm) device. The overnight bacterial culture spread onto Muller Hinton agar to obtain the final bacterial concentration 1×10^7 CFU/ml. The antibacterial properties were evaluated by measuring the zone of growth inhibition (ZOI) surrounding the substrate.

RESULTS

In this paper, the modified thermal substrate deposition method from aqueous solutions of precursors was used to obtain bioactive ZnO and ZnO/Alg coatings on the metal (Ti6Al4V) substrates. The application of this method for ZnO coatings is explained by decreasing of the ZnO powder solubility in an aqueous solution with the temperature increasing. From our testing experiments, we believe that ZnO manifests the same properties for the coatings, so the deposition and formation of ZnO nanostructured coating on the Ti6Al4V substrate occurs approximately at the same temperatures as that for ZnO powder (90-100°C). As already noted, the deposition process involves the passage of alternating current through a metal substrate immersed in an aqueous solution. As a result, the metal substrate is heated up to a temperature of 100°C due to resistive heating (Joule heating), although the hydroprocess passes under atmospheric pressure. The method of obtaining of ZnO coatings are schematically presented in Figure 1.

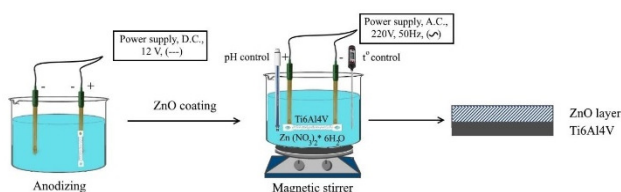


Fig. 1 Scheme for the deposition of the ZnO coating on an anodized Ti6Al4V substrate using TSD method

One of the methods for modifying the surface of a titanium implant is the formation of oxide films (TiO_2) on it by anodizing, which improves implant anticorrosion resistance. Oxide film also is characterized by high adsorption properties. In the presented paper, ZnO and ZnO/Alg coatings were deposited on an anodized titanium surface. As mentioned above, zinc oxide coatings on a titanium substrate were deposited from the polymer-containing solution (ZnO/Alg) and polymer-free solution (ZnO). Figure 2 shows the surface morphology of these coatings.

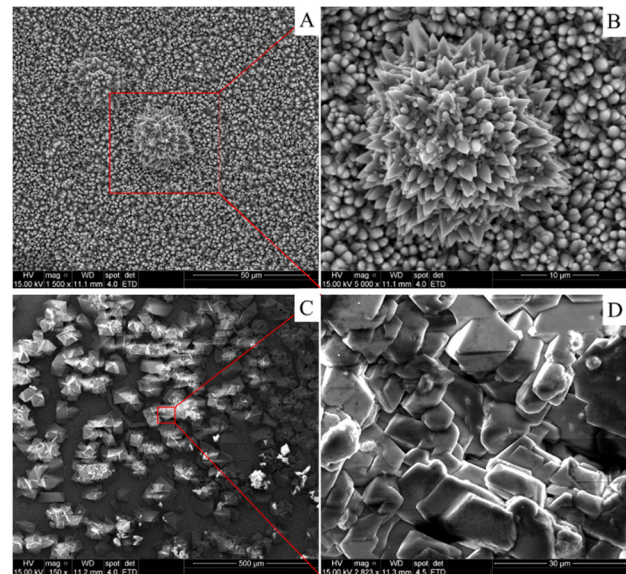


Fig. 2 Surface morphology of the coatings obtained by the TSD method on the titanium substrate: (A), (B) - ZnO at different magnifications; (C), (D) - ZnO/Alg at different magnifications

It is evident that the presence of a polymeric component sodium alginate in the mother solution significantly affects the formation of coatings, which differ in morphology. In the presence of alginate, spherical particles with flower-shaped inclusions are formed, while from the polymer-free solution, single tetrahedra-shaped crystals were obtained. The thickness of the ZnO coating deposited for 20 minutes on titanium substrate is 180 μm , while the thickness of the ZnO/Alg coating, deposited under similar conditions is 600 μm . The average rate of deposition from alginate containing solution is 30 $\mu\text{m}/\text{min}$, while from alginate-free solutions – 9 $\mu\text{m}/\text{min}$.

The X-ray diffraction patterns of the samples are present in Figure 3. The major peaks of TiO_2 and ZnO phases on the corresponding diffractograms are marked with Miller indexes. The Ti6Al4V anodized substrate diffractogram shows peaks belonging to TiO_2 (JCPDS Card No 76-0322 Rutile). Some peaks of rutile are also present on diffractograms of samples with ZnO and ZnO/Alg coatings, but the intensity of these peaks is minimal compared to that of ZnO peaks. XRD indicates the formation of an additional minor phase of Titanium Oxide Ti_3O_5 (JCPDS Card No 01-072-2101) after staying titanium substrate in alkaline conditions by the ZnO deposition. The primary phase of the coating is ZnO (JCPDS 03-0891). For both ZnO and ZnO/Alg coatings, the XRD analysis also shows the presence of the

single phase of ZnO (JCPDS 03-0891) without any additional peaks. The highest intensity peaks at (002) show that the growth direction of ZnO nanoparticles is along the c-axis for both coatings. But other peaks characteristic of the ZnO phase such as (100), (101), (102) is more intensive in the XRD pattern for ZnO/Alg compared with ZnO coating, which proves the formation of particles of different shape under the influence of polymer molecules.

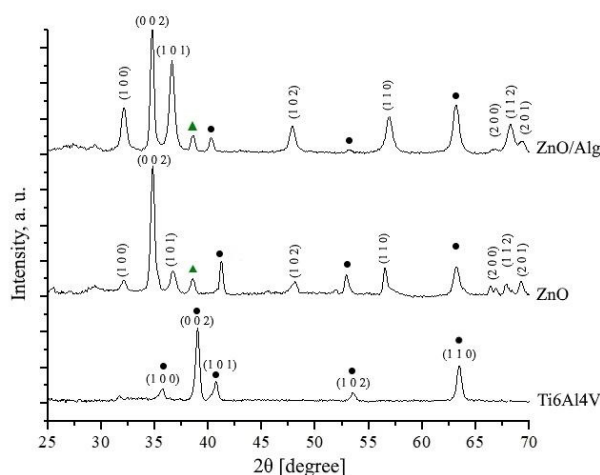


Fig. 3 Diffraction patterns from the samples: anodized titanium substrate, ZnO and ZnO/Alg coatings, deposited on titanium substrate.

The TiO_2 substrate peaks are marked with ●; titanium oxide Ti_3O_5 peaks are marked with ▲; Miller indexes indicate the peaks belonging to ZnO

The texture is present for ZnO coatings. The Harris method (Harris texture index, HTI) was used for its quantitative estimation. The crystallite sizes by Scherrer (L) were evaluated for all major peaks of the ZnO phase, as well as its unit cell parameters (a and c , nm) using (1 0 3) and (0 0 2) peaks respectively. The excellent resolution of (0 0 2) and (0 0 4) peak allowed to separate the contributions from small sizes of coherent scattering regions (L_{WH}) and the presence of microstrains (ϵ) into the peaks broadening. The separation of these contributions was performed with the Williamson–Hall method. These results are present in Table 1.

Table 1
ZnO crystal structure parameters for the coatings on the Ti6Al4V substrates obtained by the TSD method

Sample	Value	(100)	(002)	(101)	(110)	L_{WH} , nm ϵ , 10^{-3}	a, nm c, nm
ZnO	L, nm	27.3	39.3	26.3	18.0	106.0	0.325
	HTI	0.177	3.389	0.096	0.078	2.862	0.521
ZnO/ Alg	L, nm	12.0	50.8	15.7	10.3	69.6	0.322
	HTI	0.036	2.455	0.036	0.047	1.591	0.518

On the first look, the crystallinity of the ZnO phase in the ZnO coating is higher than of the ZnO/Alg, but the intensity of most peaks is higher in the case of the sample ZnO/Alg. This fact could be explained by the presence of a

higher amount of microstrains in the case of the ZnO sample, which is confirmed by their values in (0 0 1) direction. Both samples have a significant texture. HTI shows its decrease for the ZnO/Alg as compared to the ZnO. Changes in the structure are due to the influence of sodium alginate. Alginate macromolecules in the presence of divalent metal (Zn^{2+}) tend to adopt an ordered confirmation through dimerization, so they create controlled conditions for the growth of ZnO nanoparticles.

The antibacterial activity of the ZnO/Alg coating was investigated against the Gram-negative *E. coli* and Gram-positive *S. aureus* bacteria. The zone of inhibition test determined the antibacterial properties. Bacterial growth was visualized after overnight incubation of the substrates at 37°C. The diameter of the inhibition zone against the test strains was measured around the ZnO/Alg coated substrates, placed on the inoculated medium. The results of antimicrobial activity are representing in Table 2 and Figure 4. The growth inhibition zone (in mm) around coated substrates reflects the antimicrobial susceptibility of the coating. Larger the zone of inhibition, higher is the antimicrobial activity.

Table 2
Antimicrobial activity of ZnO/Alg coating against the test strains, $M \pm m$

Microorganism test - strains	Growth inhibition zone (mm) by modifying the agar diffusion method
	ZnO
<i>S. aureus</i> ATCC 25923	16.0±1.33
<i>E. coli</i> ATCC 25922	20.0±0.66

Note: $p \leq 0.05$

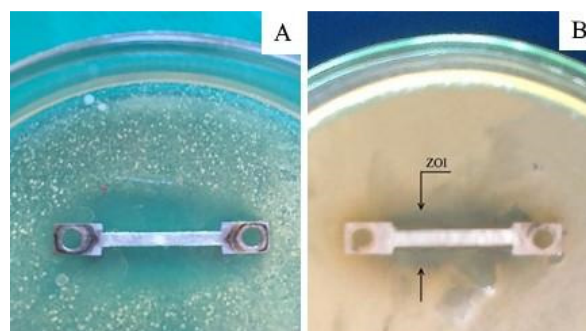


Fig. 4 Antimicrobial activity of ZnO coating against (A) *E. coli* ATCC 25922; (B) *S. aureus* ATCC 25923

Thus, it may be pointed out that ZnO nanoparticles deposited in the presence of alginate in on Ti6Al4V substrate by the TSD method demonstrated a pronounced inhibitory activity against both *S. aureus* and *E. coli* bacteria. This fact confirms the literature data that ZnO nanoparticles are characterized by increased antimicrobial activity. Although the exact antibacterial mechanism of metal nanoparticles is still incomplete, some distinctive points have been proposed, which include a formation of reactive oxygen species (ROS) on the surface of metal oxide nanoparticles, metal ion release and ion invasion into the bacterial cell wall, direct mechanical destruction of the membrane that can induce bacterial cell death.

The modern development in the field of metal implants is aimed at increasing their biocompatibility, antibacterial activity, lack of toxicity, modulation of inflammation, and fast osseointegration, which is closely related to the modern clinical demand. The results of this work are a step in this direction, namely - the creation of multifunctional implant surfaces.

CONCLUSIONS

At first, the ZnO, ZnO/Alg coatings were obtained on the pre-anodized Ti6Al4V substrates by the TSD method. It has been experimentally proved that this method can be effectively applied to obtain a zinc oxide coating on a metal surface. ZnO coatings were obtained from alginate-containing and alginate-free solutions. Natural biopolymer alginate has a significant influence on the formation of the coating, morphology, texture, structure of ZnO nanoparticles. The average rate of the ZnO deposition from alginate containing solution is 30 $\mu\text{m}/\text{min}$, while from alginate-free solutions, 6 $\mu\text{m}/\text{min}$. The thickness of the ZnO coating deposited for 20 minutes is 180 μm , while the thickness of the ZnO/Alg coating, deposited under similar conditions, is 600 μm . For this coating, an increase in the ZnO crystallites size and microstrains along the (0 0 l) direction are characteristic. The ZnO coating demonstrates growth inhibition zones around coated substrates about 16 mm for the *S. aureus* and 20 mm for the *E. coli*. The obtained coatings are promising for medical implants, based on titanium and its alloys, due to their antibacterial properties.

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REFERENCES

- [1] S.K. Aryaa, S. Sahab, J.E. Ramirez-Vickc, V. Guptab, Shekhar Bhansalid and S.P. Singh. Recent advances in ZnO nanostructures and thin films for biosensor applications: Review. *Analytica Chimica Acta* vol. 737, pp. 1-21, 2012.
- [2] D. Bian, Y. Guo and Y. Zhao Influence of Zinc Oxide on Corrosion Resistance of Alumina Based Chemically Bonded Ceramic Coatings. *Russian Journal of Applied Chemistry*, Vol. 89, No. 12, pp. 2091-2094, 2016.
- [3] P. Bhattacharjee, H. Begam, A. Chanda and S.K. Nandi. "Animal trial on zinc doped hydroxyapatite: A case study", *Journal of Asian Ceramic Societies*, vol. 2(1), pp. 44-51, 2014.
- [4] M. Chozhanathmisra, S. Ramya, L. Kavitha and D. Gopi. "Development of zinchallosyte NT/mineral substituted hydroxyapatite bilayer coatings on Ti alloy for orthopedic applications", *Colloids Surf.*, vol. 511, pp. 357-365, 2016.
- [5] R.T. Candidato Jr., R. Sergic, J. Jouina, O. Nogueraa, L. Pawłowska. Advanced microstructural study of solution precursor plasma sprayed Zn doped hydroxyapatite coatings. *Journal of the European Ceramic Society*, vol. 38, pp. 2134-2144, 2018.
- [6] L.F. Deravi, J.D. Swartz and D.W. Wright. "The biomimetic synthesis of metal oxide nanomaterials", *Wiley*, pp. 1-10, 2010.
- [7] Q. Ding, X. Zhang, Y. Huang, Y. Yan, X. Pang. In vitro cytocompatibility and corrosion resistance of zinc-doped hydroxyapatite coatings on a titanium substrate. *J Mater Sci*, vol. 50, pp. 189-202, 2015
- [8] M. Epple, "Biomaterials and biomineralization", *Wind*, p.165, 2007.
- [9] M. Farahmandjou and S. Jurablu. "Co-precipitation synthesis of zinc oxide (ZnO) nanoparticles by zinc nitrate precursor", *Int. J. Bio. Inor. Hybr. Nanomater*, vol. 3, pp. 179-184, 2014.
- [10] Z.Z. Feng, X.M. Liu, L. Tan, Z.D. Cui, X.J. Yang, Z.Y. Li, Y F. Zheng, K.W.K. Yeung and S.L. Wu. "Electrophoretic Deposited Stable Chitosan@MoS2 Coating with Rapid In Situ Bacteria-Killing Ability under Dual-Light Irradiation", *Small*, vol. 14 (21), pp. 1704347, 2018.
- [11] M.S. Gezaz, S.M. Aref, M. Khatamian, Investigation of structural properties of hydroxyapatite/ zinc oxide nanocomposites; an alternative candidate for replacement in recovery of bones in load-tolerating areas, *Mat. Chem. and Phys.* Vol. 226, pp. 169-176, 2019.
- [12] C. Jin, X. Liu, L. Tan, Z. Cui, X. Yang, Y. Zheng, K.W.K. Yeung, P.K Chu and S. Wu. "Ag/AgBr-loaded mesoporous silica for rapid sterilization and promotion of wound healing", *Bio-materials Science*, vol. 6 (7), pp. 1735-1744, 2018.
- [13] K. Kuroda, R. Ichino, M. Okido and O. Takai. "Hydroxyapatite coating on titanium by thermal substrate method in aqueous solution", *Journal of Biomedical Materials Research*, vol. 59 (2), pp. 390-397, 2001.
- [14] K. Kuroda. "Hydroxyapatite coating of titanium implants using hydroprocessing and evaluation of their osteoconductivity", *Bioinorganic Chemistry and Applications*, pp. 730693, 2012.
- [15] J. Karbowniczek, L. Cordero-Arias, S. Virtanen, S.K. Misra, E. Valsami-Jones, L. Tuchscher, B. Rutkowski, K. Gorecki, P. Bala, A. Czyska-Filemonowicz and A.R. Boccaccini. "Electrophoretic deposition of organic/inorganic composite coatings containing ZNo nanoparticles exhibiting antibacterial properties", *Mater. Sci. Eng., C* vol. 77, pp. 780-789, 2017.
- [16] J. Lva, S. Zhanga, S. Wanga, L. Luo, H. Huang and J. Zhangba State Chemical transformation of zinc oxide nanoparticles as a result of interaction with hydroxyapatite. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 461, pp. 126-132, 2014.
- [17] Y. Li, X. Liu, L. Tan, Z. Cui, X. Yang, Y. Zheng, K. Wai, K. Yeung, P.K. Chu and S. Wu. "Rapid Sterilization and Accelerated Wound Healing Using Zn2+ and Graphene Oxide Modified g-C3N4 under Dual Light Irradiation", *Advanced Functional Materials*, vol. 28 (30), pp. 1800299, 2018.
- [18] M. Moldovan, D. Prodan, V. Popescu, C. Prejmerean, C. Saroși, M. Saplonțai, S. Țălu and E. Vasile. "Structural and morphological properties of HA-ZnO powders prepared for biomaterials", *Open Chem*, vol. 13, pp. 725-733, 2015.
- [19] E. Peter Etape, J. Foba-Tendo, L.J. Ngolui, B.V. Namondo, F.C. Yollande and M.B. Nguiefack Nguimezong. Structural Characterization and Magnetic Properties of Undoped and Ti-Doped ZnO Nanoparticles Prepared by Modified Oxalate Route. *Hindawi Journal of Nanomaterials* Vol. 2018, 9072325, 9 pages.
- [20] A. Ronen, R. Semiat and C.G. Dosoretz. "Antibacterial efficiency of a composite spacer containing zinc oxide nanoparticles", *Procedia Engineering*, pp. 44581-582, 2012.

- [21] K.M. Reddy, K. Feris, J. Bell, D.G. Wingett, C. Hanley and A. Punnoose. "Selective toxicity of zinc oxide nanoparticles to prokaryotic and eukaryotic systems", *Appl Phys Lett*, vol. 90, pp. 1-3, 2007.
- [22] K.R. Rasmis, S.C. Vanithakumari, R.P. George and U. Kamachi Mudali. "Active Nano Metal Oxide Coating for Bio-fouling Resistance", *Trans Indian Inst Met*, vol. 71 (6), p. 1323-1329, 2018.
- [23] M. Roknian, A. Fattah-alhosseini, S.O. Gashti and M.K. Keshavarz. "Study of the effect of ZnO nanoparticles addition to PEO coatings on pure Ti substrate: microstructural analysis, antibacterial effect and corrosion behavior of coatings in Ringer's physiological solution", *J. Alloys Compd.* vol. 740, pp. 330-345, 2018.
- [24] L.F. Sukhodub, L.B. Sukhodub, W. Simka and M. Kumeda. "Hydroxyapatite and brushite coatings on plasma electrolytic oxidized Ti6Al4V alloys obtained by the thermal substrate deposition method", *Materials Letters*, vol. 250, pp. 163-166, 2019.
- [25] L. Sukhodub, A. Panda, L. Sukhodub, M. Kumeda, K. Dyadyura and I. Pandová. "Hydroxyapatite and zinc oxide based two-layer coating, deposited on ti6al4v substrate", *MM Science Journal*, pp. 3494-3499, (2019).
- [26] R. Sergia, D. Bellucci, R.T. Candidato Jr, L. Lusvarghi, G. Bolelli, L. Pawlowski, G. Candiani, L. Altomare, L. De Nardo and V. Cannillo. Bioactive Zn-doped hydroxyapatite coatings and their antibacterial efficacy against *Escherichia coli* and *Staphylococcus aureus*. *Surface & Coatings Technology*, Vol. 352, pp. 84-91, 2018.
- [27] S. Spriano, S. Yamaguchi, F. Baino and S. Ferraris. "A critical review of multifunctional titanium surfaces: New frontiers for improving osseointegration and host response, avoiding bacteria contamination", *Acta Biomater.* vol. 79, pp. 1-22, 2018.
- [28] S. Stankic, S. Suman, F. Haque and J. Vidic. "Pure and multi metal oxide nanoparticles: synthesis, antibacterial and cytotoxic properties", *J Nanobiotechnol.*, vol. 14, pp. 73, 2016.
- [29] L. Tan, J. Li, X. Liu, Z. Cui, X. Yang, K. Wai, K. Yeung, H. Pan, Y. Zheng, X. Wang and S. Wu. "Thermal-Triggered Release from Black Phosphorous with Strengthened Chemical Stability", *Small*, vol. 14 (9), pp. 1703197, 2018.
- [30] R.K. Thareja and S. Shukla. "Synthesis and characterization of zinc oxide nanoparticles by laser ablation of zinc in liquid", *Appl. Surf. Sci.*, vol. 253, pp. 8889-8895, 2007.
- [31] X. Xie, C. Mao, X. Liu, L. Tan, Z. Cui, X. Yang, S. Zhu, Z. Li, X. Yuan, Y. Zheng, K.W.K. Yeung, P.K. Chu and S. Wu. "Tuning the Bandgap of Photo-Sensitive Polydopamine/Ag3PO4/Graphene Oxide Coating for Rapid, Noninvasive Disinfection of Implants", *ACS Central Science*, vol. 4(6), pp. 724-738, 2018.
- [32] A. Yanovska, V. Kuznetsov, A. Stanislavov, S. Danilchenko and L. Sukhodub. "Synthesis and characterization of hydroxyapatite-based coatings for medical implants obtained on chemically modified Ti6Al4V substrates", *J. Surf. Coat. Technol.*, vol. 205, pp. 5324-5329, 2011.
- [33] A. Yanovska, V. Kuznetsov, A. Stanislavov, S. Danilchenko and L. Sukhodub. "A study of brushite crystallization from calcium-phosphate solution in the presence of magnesium under the action of a low magnetic field", *Materials science and engineering C*, vol. 32, pp. 1883-1887, 2012.
- [34] Z.Z. Feng, X.M. Liu, L. Tan, Z.D. Cui, X.J. Yang, Z.Y. Li, Y.F. Zheng, K.W.K. Yeung and S.L. Wu. "Electrophoretic Deposited Stable Chitosan@MoS2 Coating with Rapid In Situ Bacteria-Killing Ability under Dual-Light Irradiation", *Small*, vol. 14 (21), pp. 1704347, 2018.
- [35] X. Zhang, H. Wang, J. Li, X. He, R. Hang, X. Huang, L. Tian, B. Tang. "Corrosion behavior of Zn-incorporated antibacterial TiO2 porous coating on Ti", *Ceram. Int.*, vol. 42, pp. 17095-17100, 2016.
- [36] Y. Zhang, X. Liu, Z. Li, S. Zhu, X. Yuan, Z. Cui, X. Yang, P. K Chu and S. Wu. "Nano Ag/ZnO Incorporated Hydroxyapatite Composite Coatings: Highly Effective Infection Prevention and Excellent Osteointegration", *ACS Applied Materials & Interfaces*, p. 1-46, 2018.
- [37] A. Panda, J. Duplak, J. Jurko and M. Behun. "Comprehensive Identification of Sintered Carbide Durability in Machining Process of Bearings Steel 100CrMn6", *Advanced Materials, Research*, vol. 340, pp. 30-33, 2011.
- [38] A. Panda, K. Dyadyura, J. Valicek, M. Harnicarova, J. Zajac, V. Modrak, I. Pandova, P. Vrabel, E. Novakova-Marcincinova and Z. Pavelek. "Manufacturing Technology of Composite Materials – Principles of Modification of Polymer Composite Materials Technology Based on Polytetrafluoroethylene". *Materials*, vol. 10, no. 4, pp. 337, 2017.
- [39] J. Valicek, M. Harnicarova, A. Panda, I. Hlavaty, M. Kusnerova, H. Tozan, M. Yagimli and V. Vaclavik. "Mechanism of Creating the Topography of an Abrasive Water Jet Cut Surface". *Machining, joining and modifications of advanced materials*, vol. 61, pp. 111-120, 2016.
- [40] A. Panda, Š. Olejárová, J. Valíček and M. Harničárová. "Monitoring of the condition of turning machine bearing housing through vibrations". *International Journal of Advanced Manufacturing Technology*, vol. 97, no. 1-4, pp. 401-411, 2018.
- [41] J. Valicek, M. Harnicarova, I. Kopal, Z. Palková, M. Kušnerová, A. Panda and V. Šepelák. "Identification of Upper and Lower Level Yield strength in Materials". *Materials*, vol. 10, no. 9, pp. 1-20, 2017.
- [42] A. Panda, J. Dobránský, M. Jančík, I. Pandová and M. Kačalová. "Advantages and effectiveness of the powder metallurgy in manufacturing technologies". *Metallurgija*, vol. 57, no. 4, pp. 353-356, 2018.
- [43] J. Valicek, M. Harnicarova, I. Hlavaty, R. Grznárik, M. Kusnerova, Z. Mitařová and A. Panda. "A new approach for the determination of technological parameters for hydroabrasive cutting of materials". *Materialwissenschaft und Werkstofftechnik*, vol. 47, pp. 462-471, 2016.
- [44] I. Pandova, T. Gondova and K. Dubayova. "Natural and Modified Clinoptilolite Testing for Reduction of Harmful Substance in Manufacturing Exploitation". *Advanced Materials Research*, vols. 518-523, pp. 1757-1760, 2012.
- [45] J. Macala, I. Pandova, T. Gondova and K. Dubayova. "Reduction of polycyclic aromatic hydrocarbons and nitrogen monooxide in combustion engine exhaust gases by clinoptilolite". *Gospodarka Surowcami Mineralnymi*, vol. 28, no. 2, pp. 113-123. 2012.
- [46] J. Macala, I. Pandova and A. Panda. "Zeolite as a prospective material for the purification of automobile exhaust gases". *Mineral resources management*, vol. 33, no. 1, pp. 125-138. 2017.
- [47] J. Macala, I. Pandova and A. Panda. "Zeolite as a prospective material for the purification of automobile exhaust gases". *Mineral resources management*, vol. 25, no. 4, pp. 23-32. 2009.
- [48] A. Panda, V. Nahornyi, I. Pandová, M. Harničárová, M. Kušnerová, J. Valíček and J. Kmec. "Development of the method for predicting the resource of mechanical systems". *International Journal of Advanced Manufacturing Technology*, vol. 105, no. 1-4, pp. 1563-1571, 2019.

- [49] M. Balara, D. Duplakova and D. Matiskova. "Application of a signal averaging device in robotics 2018". *Measurement*, vol. 115, pp. 125-132, 2018.
- [50] M. Durdan, B. Stehlikova, M. Pastor, J. Kacur, M. Laciak and P. Flegner. "Research of annealing process in laboratory conditions". *Measurement*, vol. 73, 2015, pp. 607-618. ISSN 0263-2241.
- [51] K. Monkova and P. Monka. "Some aspects influencing production of porous structures with complex shapes of cells". *Lecture Notes in Mechanical Engineering*, pp. 267-276, 2017.
- [52] S. Olejarova, J. Dobransky, J. Svetlik and M. Pituk. "Measurements and evaluation of measurements of vibrations in steel milling process". *Measurement*, vol. 106, pp. 18-25, 2017. ISSN 0263-2241.
- [53] M. Rimar, M. Fedak, A. Kulikov and P. Smeringai. "Study of gaseous flows in closed area with forced ventilation." *MM Science Journal*, vol. 2018, no. March, pp. 2188-2191, 2018.
- [54] J. Dobránsky, M. Pollák and Z. Doboš. "Assessment of production process capability in the serial production of components for the automotive industry". *Management systems in production engineering*, vol. 27, no. 4, pp. 255-258, 2019.
- [55] M. Pollák, J. Torok, J. Zajac, M. Kočíško and M. Teliskova. "The structural design of 3D print head and execution of printing via the robotic arm ABB IRB 140". *ICIEA 2018*, vol. 2018, pp. 194-198, 2018.
- [56] W. Bialy and J. Ružbarský. "Breakdown cause and effect analysis. Case study". *Management systems in production engineering*, vol. 26, pp. 83-87, 2018.
- [57] D. Duplakova, L. Knapcikova, M. Hatala and E. Szilagyi. "Mathematical modelling of temperature characteristics of RFID tags with their subsequent application in engineering production". *TEM Journal-Technology Education Management Informatics*, vol. 5, pp. 411-416, 2016.
- [58] J. Kascak, P. Baron, M. Teliskova, J. Zajac, J. Torok and J. Husar. "Implementation of augmented reality into the training and educational process in order to support spatial perception in technical documentation". *6th IEEE international conference on industrial engineering and applications*, pp. 583-587, 2019.
- [59] R. Bielousova. "Developing materials for english for specific purposes online course within the blended learning concept". *TEM Journal-Technology Education Management Informatics*, vol. 6, pp. 637-642, 2017.
- [60] Ľ. Straka, I. Čorný and J. Piteľ. "Properties evaluation of thin microhardened surface layer of tool steel after wire EDM". *Metals*, vol. 6, no. 5, pp. 1-16, 2016.
- [61] Ľ. Straka, I. Čorný and J. Piteľ. "Prediction of the geometrical accuracy of the machined surface of the tool steel EN X30WCrV9-3 after electrical discharge machining with CuZn37 wire electrode". *Metals*, vol. 7, no. 11, pp. 1-19, 2017.

Leonid Sukhodub

ORCID ID: 0000-0002-1559-0475

Sumy State University, Medical Institute,
2, Rymskogo-Korsakova st., 40007 Sumy, Ukraine
e-mail: L.sukhodub@gmail.com

Luidmila Sukhodub

ORCID ID: 0000-0002-9350-5766

Sumy State University, Medical Institute,
2, Rymskogo-Korsakova st., 40007 Sumy, Ukraine

Mariia Kumeda

ORCID ID: 0000-0002-8480-9223

Sumy State University, Medical Institute,
2, Rymskogo-Korsakova st., 40007 Sumy, Ukraine

Anton Panda

ORCID ID: 0000-0002-1759-7355

Technical University of Kosice
Faculty of Manufacturing Technologies
Sturova 31, 08001 Presov, Slovak Republic
e-mail: anton.panda@tuke.sk

Petr Baron

ORCID ID: 0000-0002-4789-529X

Technical University of Kosice
Faculty of Manufacturing Technologies
Sturova 31, 08001 Presov, Slovak Republic