Development and Characterization of Multilayered Cu/HA/ZnS+PEEK Coating System by Hybrid Technology



FILIP KUŚMIERCZYK, ŁUKASZ CIENIEK, AGNIESZKA KOPIA, SŁAWOMIR ZIMOWSKI, and TOMASZ MOSKALEWICZ

In this study, multilayered Cu/HA/ZnS + PEEK coatings were fabricated using hybrid technology on Zr–2.5Nb alloy substrates. The use of electrophoretic deposition (EPD) and heat treatment allowed the 1st base composite ZnS + PEEK layer and the 2nd hydroxyapatite (HA) top layer to be obtained. The EPD kinetics of both layers was studied. Heating at a temperature of 450 °C and slow cooling resulted in densification and sulfonation of PEEK. It also led to an increase in the adhesion of HA particles on the surface of the PEEK + ZnS layer and to the settlement of HA particles deep into the 1st layer. The effect of substrate preparation on the adhesion strength of coatings was investigated. The ZnS + PEEK layer exhibited high adhesion to the chemically treated zirconium alloy. Furthermore, the first layer was characterized by a high scratch resistance. The selective distribution of Cu on the top of the coating was obtained by shadow-masked pulsed laser deposition (PLD). The multilayered coatings exhibited high roughness and mild hydrophobicity. This study showed the possibility of obtaining a multilayered coating system with a controlled distribution of bioactive components (HA) and antimicrobial components (Cu) on its surface using a hybrid method that combined EPD, heat treatment, and PLD.

https://doi.org/10.1007/s11661-023-07057-1 © The Author(s) 2023

I. INTRODUCTION

ZIRCONIUM alloys belong to a group of metallic biomaterials that are commonly used for bone implants. Due to their exceptional electrochemical corrosion resistance, wear resistance and low modulus of elasticity (roughly 90 GPa), which is lower than that of stainless steels, cobalt alloys and two-phase $\alpha + \beta$ titanium alloys, they are widely studied and used as orthopedic and dental implants.^[1,2] In addition, zirconium alloys display higher biocompatibility than steels, cobalt and titanium alloys.^[3] One of the most perspective alloys is Zr-2.5Nb, which reveals favorable biocompatibility, high electrochemical corrosion resistance and acceptable mechanical properties.^[4] Although zirconium alloys are coated with a passive layer of ZrO₂, which exhibits rather moderate bioactivity, their osteoinductivity must be enhanced.^[5–7] This can be achieved by employing composite coatings with a bioactive component.

METALLURGICAL AND MATERIALS TRANSACTIONS A

One of the excellent composite coating matrix materials is polyetheretherketone (PEEK). It is characterized by remarkable resistance to chemicals and radicals, high stability, mechanical strength and wear resistance.^[8] In addition, PEEK exhibits an elasticity modulus close to that of human trabecular bone, much less than that of metallic biomaterials. Therefore, its use in the coating can decrease the effects of stress shielding on the surrounding bone. Due to its superior properties, it is often used as spinal, dental and orthopedic implants or medical equipment.^[9–11] Although it is characterized by biological inertia.^[12] Due to this drawback, it is necessary to incorporate bioactive and antiseptic agents in PEEK-based coatings.

One of the most well-known biologically active factors is synthetically prepared hydroxyapatite (HA), with a chemical composition of $Ca_{10}(PO_4)_6(OH)_2$.^[13] This ceramic is one of the main components of natural bones. HA is widely applied in bioactive coatings and scaffolds because it can form a chemical bond with the bone.^[14] Due to its bioactivity, osteoconductivity, biocompatibility and ability to form a stable connection with osseous tissue, it is widely used for bone repair.^[15,16] Although there are numerous advantages, HA is easily agglomerated and brittle. Therefore, it is often used in composite coatings as an additional bioactive component. When incorporated into the

FILIP KUŚMIERCZYK, ŁUKASZ CIENIEK, AGNIESZKA KOPIA, and TOMASZ MOSKALEWICZ are with the Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology, al. Mickiewicza 30, 30-059, Kraków, Poland. Contact e-mail: kusmierczyk@agh.edu.pl SLAWOMIR ZIMOWSKI is with the Faculty of Mechanical Engineering and Robotics, AGH University of Science and Technology, al. Mickiewicza 30, 30-059, Kraków, Poland.

coating, it is able to increase the concentration of local Ca^{2+} ions concentration, stimulating bone forma-tion.^[17,18] Despite this advantage, HA induces a bone growth effect, but does not prevent the formation of bacterial microfilms. Hence, antibacterial ingredients are often applied in composite biomaterials containing HA. During osseointegration processes, it is very important to inhibit the development of biofilm, which can cause serious infection. This behavior can not only be a cause of implant repudiation, but also be a threat to patient health.^[19,20] The currently investigated and promising antibacterial ingredients include ZnS and Cu nanoparticles. ZnS is characterized by antimicrobial activity, relatively high chemical stability, and non-toxicity. Therefore, it is suitable for use in coatings.^[21,22] Furthermore, as reported in our previous study,^[23] ZnS provides a source of sulfur for the thermal sulfonation process of PEEK. Sulfonated PEEK (S-PEEK) enhances bone cell formation on the coatings,^[24,25] as well as exhibits antibacterial activity.^[26] Accordingly, the use of ZnS particles in the coating composition is doubly beneficial. Copper is one of the most important microelements in the human body. The antibacterial activity of this element is known and widely used.^[27-29] Despite the negligible reactivity of Cu to human tissues, it is highly effective against harmful microorganisms. From the perspective of the decline in the effectiveness of the most widely used antibiotics, the use of Cu nanoparticles is a promising alternative.^[30,31]

Electrophoretic deposition (EPD) is widely applied and studied for the deposition of polymer-based coatings with the addition of various bioactive ceramics, including HA.^[32–34] EPD is accomplished via the movement of particles suspended in a liquid medium under an electric field. The conductive substrate is used as the working electrode and is coated by particles of opposite charge. This method is advantageous due to the short time of deposition and the limited restriction of the substrate shape. Furthermore, for the densification of PEEK coatings, thermal treatment is neces-sary.^[23,32,33,35–38] Multilayered coatings often require the use of multiple suspensions during EPD and repeating individual deposition operations. However, they allow for limited control of the location of individual components. PEEK-based coatings with both antimicrobial and bioactive agents were previously obtained only in a few studies.^[23,33,39–42] Seuss *et al.*^[39] developed PEEK coatings containing HA and Ag particles. Abdulkareem et al.^[40] achieved PEEK coatings with the addition of HA and chitosan. In our previous studies, multicomponent HA/MoS₂/PEEK and HA/ZnS/PEEK coatings were successfully deposited.^[23,33] However, efficiently all of the above coatings were obtained as single-layered. Although potentially beneficial, the multilayered EPD technique was applied for the development of PEEK-based composites on a limited basis. Virk *et al.*^[41] developed multilayered PEEK-based coatings with curcumin, hexagonal boron nitride and bioactive glass. Moreover, Ur Rehman^[42] obtained a bioactive glass (BG)/chitosan layer loaded

with lawsone on the base layer of PEEK/BG. Nevertheless, no studies have been reported on the hybrid method involving EPD and selective pulsed laser deposition (PLD) for obtaining multilayered coatings with fully controlled distribution of antibacterial and bioactive agents. Physical vapour phase deposition using masking is a very promising technique for selective deposition of Cu "island structures" on any substrate.[43] This technique provides numerous advantages, including high precision, speed and efficiency of deposition, tight control of the deposited structure and high flexibility.^[43,44] A significant benefit of using PLD is the preservation of the phase composition and stoichiometry of the deposited materials. Shadow masking is often used as a factor to reduce the occurrence of coating defects, such as droplets, which are micrometersized particles that can have a negative impact on coating properties, which is related to mask displacement along the target-substrate path and verification of the deposition rate.^[44,45] In the present work, the selective Cu deposition process was carried out with the mask attached directly to the samples, which is a new approach. PLD with a shadow mask enables selective deposition of Cu "islands" of desired size, thickness and precise distribution within the bioactive coating matrix and thus can regulate the biological response of both cells and bacteria. The present work focuses on the development of multilavered Cu "islands"/HA/ZnS + PEEK coatings by a hybrid method consisting of EPD, heat treatment (HT) as well as shadow masked PLD on Zr-2.5Nb alloy substrates. The parameters of the processes, including EPD kinetics, were optimized and studied. The resulting coatings were studied in terms of morphology and microstructure, surface topography, scratch resistance, and adhesion strength.

II. EXPERIMENTAL

A. Materials

The Zr-2.5Nb alloy used as substrates for coating deposition was supplied by Luoyang Dingding Tungsten and Molybdenum Materials Co., Ltd. (China). The alloy microstructure was described in our previous study.^[23] It consisted mainly of α platelets with hexagonal closed packed (hcp) structure in β grains with body centered cubic (bcc) structure and size (equivalent circle diameter, ECD) in the range of 50 to 500 μ m. Substrate discs with a thickness of 3 mm were cut from the rod with a diameter of 20 mm. The discs were ground using 600-grit sandpaper. After that, the discs were additionally chemically or thermally treated. Chemical treatment was applied with the use of 45 ml of HNO₃, 5 ml of HF and the rest of distilled H₂O up to 100 ml according to Kuran *et al.*^[46] after etching for 5 minutes and soaking in distilled water. Thermal treatment consisted of heating for a duration of 2 hours at 550 °C and cooling with a furnace with the use of a Czylok MRT-20 laboratory furnace (Poland) as described by Luo *et al.*^[4]



Fig. 1-Scheme of particular stages of multilayer Cu/HA/ZnS + PEEK coating fabrication.

PEEK powder (VICOTE 704) provided by Victrex Europa GmbH Germany. The particles exhibited irregular shape with an ECD of 2 to 15 μ m, as described elsewhere.^[32,38]

ZnS nanoparticles with size up to 100 nm were supplied by Nanoshell UK Ltd. They exhibited globular and oblong shapes with ECD in the range of 40 to 440 nm, as well as included both the hexagonal primitive (hp) phase and the rhombohedral primitive (rp) phase.^[23]

The HA nanoparticles produced by the Institute of High Pressure Physics of the Polish Academy of Sciences had a mean size of 10 nm, according to the supplier. Fine needle-shaped HA particles with a Ca: P atomic ratio of approximately 1.80 were 20 to 120 nm long and approximately 5 nm wide, as described elsewhere.^[23] The high purity copper (Cu) sputtering target (purity: 99.99 pct) was used as a target in the PLD process to produce "islands" on the surface of the multilayered system.

B. Multilayered Coating Deposition and Treatment

The 1st base ZnS + PEEK and 2nd HA layers of multilayered coatings were fabricated by EPD and heat treatment. The outer Cu 'islands' were deposited by PLD. The successive stages of the fabrication of successive layers in a multilayer coating are shown schematically in Figure 1.

The suspension used for the EPD of the 1st layer contained 30 g/L of PEEK 704 and 0.4 g/L of ZnS. A mixture of pure ethanol and chitosan polyelectrolyte (CHp) was used as the dispersion phase in amounts of 95 and 5 vol pct, respectively. CHp consisted of 0.5 g/Lchitosan powder dissolved in 1 pct vol. acetic acid and distilled water by mixing at 650 rpm for 3 days at room temperature (23 °C) with a magnetic stirrer (IKA RO 5, Germany). After adding powders to the ethanol-CHp dilution, it was stirred for 10 minutes and ultrasonically dispersed for 20 minutes to break down the agglomerates of particles. The suspension used for the EPD of the HA layer contained 10 g/L of HA in pure ethanol (99.8 pct purity). Directly before deposition, it was mixed and dispersed for 10 minutes, respectively. The pH of the suspensions obtained was 5.39 and 8.14 for those containing ZnS and PEEK and for those containing HA, respectively.

The two-electrode system was used for the EPD process with the application of an EX752M Multi-mode PSU power supply (UK) as a source of direct current

(DC). The zirconium alloy was engaged as the working electrode, and an austenitic stainless steel plate was employed as the counter electrode. The distance between the electrodes was 10 mm. The counter electrode was cleaned with distilled water and ethanol before deposition. A constant voltage in the range of 10 to 150 V (with a change of 20 V) and a stable deposition time of 15 and 30 seconds were applied for the EPD of the ZnS + PEEK and HA layers, respectively. After deposition of the 1st layer, the suspension was changed and the 2nd layer was deposited without voltage change. During the process, the change in current density was recorded by Multimeter Tektronix DMM 4040 (USA). The EPD yield and rate of particles were investigated for processes performed at a constant voltage of 90 V and different times of 5, 10 and 15 seconds for the 1st layer, as well as 10, 20 and 30 seconds for the 2nd layer. Sample weight analysis was carried out with the use of an analytical weight of Ohaus Europe GmbH (Switzerland). Samples with two-layer coatings were subjected to heat treatment with the use of a Czylok MRT-20 laboratory furnace (Poland). The treatment consisted of heating at a temperature of 450 °C for 30 minutes (with a heating rate of 15 °C/min and a cooling rate of 2 °C/min) in an air atmosphere.

To produce island structures of pure copper on a predefined composite surface, a laser ablation system (PLD process) consisting of two main components was used. It involved a steel vacuum chamber and a pulsed solid-state Nd:YAG laser (LOTIS Tii LS-2147). A laser beam with a wavelength of 1064 nm and output energy of 0.84 J (pump energy~60 J) was directed to the surface of the rotating Cu target through an optical path: a curving prism, a focusing lens and a quartz window in the chamber. A typical consequence of this transfer is a limitation of the beam characteristics. The specifications of the single pulse measured at the target surface were as follows: spot diameter ~1.6 mm, energy ~0.271 J, energy density 13.5 J/cm². The repetition rate of 10 Hz, a gas atmosphere of 40 mTorr Ar (~530 mbar) and a total number of pulses of 325,000 were other parameters of the deposition process. The shadow mask was made of stainless 316L steel with an aperture diameter of 45 μ m.

C. Characterization: Microstructure and Surface Topography

Examination of the morphology and microstructure of coatings was conducted with the use of a light microscope (LM) OPTA-TECH SK (Poland), scanning electron microscope (SEM) FEI Nova NanoSEM 450 (the Netherlands) and transmission electron microscope (TEM) FEI TECNAI TF 20 X-TWIN (the Netherlands). The microstructure of the coatings on the crosssection was investigated on lamellae prepared by a focused ion beam (FIB) using an FEI QUANTA 3D 200i device (the Netherlands). Electron diffraction in TEM and X-ray diffractometry (XRD) in Bragg– Brentano arrangement using a Panalytical Empyrean DY1061 diffractometer (UK) were employed for phase analysis. JEMS diffraction simulation software (Switzerland) was used for the interpretation of selected area electron diffraction patterns. The chemical composition of the coatings was investigated using energy-dispersive X-ray spectroscopy (EDS) microanalysis.

The roughness of the coating surface was investigated with a WYKO NT930 optical profilometer (USA). Several images taken at various locations on the samples surface of areas with dimensions of $900 \times 1300 \ \mu m$ were analyzed with Vision (USA) software.

The thickness of the multilayer coating and its component layers in the subsequent stages of the deposition process, both before and after heat treatment, was measured using the non-contact method using a Profilm 3D optical profilometer from Filmetrics, USA.

D. Characterization: Selected Properties

The interfacial free energy (IFE) and wetting angle (WA) were investigated by applying polar (distilled water) and nonpolar liquid (diiodomethane) to the surface of the coating with the use of a Krüss DSA25E goniometer (Germany). The examination was repeated 10 times with the use of 10 drops of nonpolar and polar liquid. On the basis of the obtained data, the IFE value was calculated by the Owens–Wendt–Rabel–Kaelble (OWRK) method.

Adhesion tests were performed with the use of an Elcometer cross-cutting knife (Germany) based on ASTM D3359B. A cross-cut was made in the coating, and then the tape was placed and subsequently torn off after 90 seconds. Observation of the sample surface after the tests was performed with the naked eye, LM, and SEM. The results of the tests were examined on the basis of the removed coating area according to the standard adhesion table in ASTM D3359B.

The Micro Combi Tester (Switzerland) was utilized for the micro-scratch tests. A Rockwell C diamond stylus with an apex angle of 120 deg and a tip radius of 200 μ m was applied for the testing. Linear increasing loads from 0.01 N were applied to 30 N with a scratching speed of 5 mm/min and a length of 5 mm were applied. The Oliver and Pharr technique of instrumental indentation technique^[47] was used for investigating the microhardness and elastic modulus of the coatings. In indentation tests, the Vickers indenter penetrated the coatings with a load of 100 mN, as well as a constant loading and unloading rate of 200 mN/ min. The dwelling time with the use of maximum load lasted 15 seconds. The measurements were repeated with a minimum number of repetitions of ten times, each time in varying areas of the coating.

III. RESULTS AND DISCUSSION

Based on our previous studies^[23,33] CHp was used for electrosteric stabilization of the suspension and codeposition of ZnS and PEEK particles on the cathode. Previous studies of the zeta potential (ZP) of PEEK, HA, and ZnS particles in pure ethanolic alcohol and the alcohol with the addition of 5 vol pct CHp, showed that the CHp provides positive values of ZP for a pH range of 3.0 to 12.0.^[23] It is most crucial for PEEK particles, for which the isoelectric point (slightly above 5.5 pH) in pure EtOH is very adjacent to the isoelectric point of the suspension of ZnS + PEEK with CHp (5.4 pH), which could significantly impede cathodic deposition. The EPD of the HA layer was carried out from a pure EtOH suspension due to the wide range of positive ZP values from 3.0 to 8.5 pH, with an isoelectric point of 8.75 pH. The pH value of the suspension was 8.14 at RT.

A short deposition time of 15 seconds was enough to obtain a sufficiently thick homogeneous ZnS + PEEK layer as the base for the second HA layer. The influence of voltage on the homogeneity of the layer was visible with the unaided eye, as well as with the use of SEM. The SEM investigation of the as-deposited first layer of ZnS + PEEK confirmed that the deposition voltage of 30 V during 15 seconds is not sufficient to obtain a homogenous coating that completely covers the underlying substrate (Figure 2(a)). Deposition in the voltage range of 30 to 70 V at the same time resulted in the achievement of a non-uniform thin layer. Observed with the unaided eye, the ZnS + PEEK layer deposited at a voltage between 70 and 110 V was satisfactory thick, with the presence of open pores. EPD at higher voltages (90, 150 V) led to the acquisition of continuous coatings that covered the substrate material (Figures 2(b) and (c)). The microscopic surface morphology of the coatings deposited with the voltage of 90 and 150 V was similar and contained numerous open pores with the ECD up to 20 μ m, which were relatively homogeneously distributed on the surface. Furthermore, microcracks up to 100 µm long were visible on both coatings, although they were slightly more apparent on the surface of the coating developed at 150 V. The coatings deposited at voltages higher than 110 V were macroscopically inhomogeneous with numerous pores, and the number of inconsistencies multiplied with increasing voltage. During the EPD of the second layer (HA), no deposition was observed on the surface of the ZnS + PEEK below 50 V, as observed with the naked eye. The SEM-EDS investigation of the HA layer obtained with the use of 30 V revealed the deposition to a very limited extent (Figure 3(a)). Almost no change in surface morphology was observed compared to that of the base ZnS + PEEKlayer. Inspecting macroscopically, in the voltage range of 50 to 70 V, single HA agglomerates were obtained. On the contrary, macroscopically, deposition above 110 V resulted in massive and uneven HA agglomeration. The SEM and SEM-EDS investigation revealed that the selective HA coating developed at 90 and 150 V on the surface of ZnS + PEEK was clearly visible (Figures 3(b) and (c)). The presence of pores on the



Fig. 2—Surface morphology of the ZnS + PEEK layers after deposition at 30 V (*a*), 90 V (*b*) and 150 V (*c*) and constant deposition time of 15 s, SEM.

surface of these coatings was limited. Nevertheless, microcracks with lengths up to 220 μ m were visible. The surface morphology of the coating with HA deposited at 150 V was more diversely developed, with increased HA agglomeration. Therefore, EPD in the voltage range from 70 to 110 V was applied to achieve the HA layer.

Examination of the change in current density of the ZnS + PEEK layer deposition exhibited its fluctuations for a voltage of 90 and 150 V for the first 5 seconds of the process (Figure 4(a)). After that, the process was stable. For 30 V, the change in current density was without fluctuations. For the deposition voltage of 90 V, the current density was stable at 0.54 mA/cm^2 . The instability of the current density was reflected in the macroscopic unevenness and noticeable thickness of the coatings deposited with the voltage of 150 V. They were characterized by numerous pores and irregularities. Unlike coatings deposited at 30 V in which no inconsistencies were observed, although they were thin. Coatings deposited at 90 V had limited pores and uniformly covered the substrate. As for the HA layer, the change in current density for voltage values of 30, 90 and 150 V was relatively similar, ranging from 0.005 to 0.02 mA/cm^2 for the entire deposition time of 30 seconds (Figure 4(b)). The current density for the three voltages was meagre due to the presence of an insulating ZnS + PEEK layer. Interestingly, in contrast to the ZnS + PEEK layer, the change in current density was the highest for a deposition voltage of 30 V and oscillated at around 0.018 mA/cm². The current density change for deposition at 150 V peaked at 0.0085 mA/cm², but the average value most of the time was about 0.008 mA/cm². For the EPD at 90 V, the current change was in the range of 0.007 to 0.017 mA/cm².

Moreover, the EPD kinetics, deposition yield and rate of both layers were investigated. The deposition yield of the ZnS + PEEK layer was growing fast and almost linearly and peaked close to 0.06 mg/mm² at the end of the layer deposition (15 seconds) (Figure 5(a)). The deposition yield of the HA layer also increased with the linear progress of the deposition, but was slower, reaching 0.03 mg/mm² at 30 seconds (Figure 5(a)). Regarding the deposition rate of the ZnS + PEEK layer it increased promptly during the first 5 seconds of the deposition reaching 0.004 mm/mg²·s, then decreased to 0.0035 mm/mg²·s in the 10th second, reaching the final value of 0.004 mm/mg²·s in the 15th second. The deposition rate of the HA layer on the underlying ZnS



Fig. 3—Surface morphology of the HA/ZnS + PEEK layers after EPD of the HA layer (without heat treatment) at 30 V (a), 90 V (b) and 150 V (c) during constant time of 30 s, SEM.

+ PEEK expanded significantly until the 10th second of deposition up to 0.001 mm/mg²·s and then stabilized at this value until the end of the process. The lower deposition rate and yield of the HA layer were a result of the occurrence of a non-conductive continuous ZnS + PEEK layer on the conductive substrate. It was observed that the HA nanoparticles were deposited preferably in areas of the lower thickness of the ZnS + PEEK layer, such as open pores, because of the lesser insulation effect. Similarly, Virk *et al.*^[41] and Ur Rehmann *et al.*^[42] reported that the second layers of curcumin/chitosan and bioactive glass/chitosan, respectively, filled the open pores of the PEEK-based layer.

Based on the heat treatment parameters of singlelayered multicomponent HA/ZnS/PEEK and HA/ $MoS_2/PEEK$ coatings used in our previous works,^[23,33,48] the coated substrates were heat treated at 380 °C and 450 °C for 30 minutes and then cooled with the furnace. The temperature of 380 °C was found to be not sufficient for the PEEK sulfonation and its partial crystallization was found (Figure 6(a)). In contrast, the coatings obtained at 450 °C exhibited an amorphous PEEK structure indicating that the sulfonation process took place (Figure 6(b)). Moreover, both

patterns validated the presence of ZnS (hp) and ZnS (rp). Although the thermal decomposition temperature of ZnS is about 650 °C,^[49] the lower temperature of the heat treatment (450 °C) of the coatings in the air environment was selected due to the degradation of PEEK, which takes place above 575 °C.^[50] The results of the XRD investigation performed in the present work and the FTIR investigation described in our previous work^[23] indicate that PEEK sulfonation occurred under the conditions mentioned above. We suppose that this process is due to a partial decomposition of sulfides, which is probably sufficient to substitute the PEEK chemical chain with sulfur. Due to the lower temperature of applied heat treatment compared to the thermal decomposition temperature of ZnS, this phase is still present in the PEEK matrix, similar to our previous research on multicomponent n-HA/ZnS/PEEK coatings.^[23] Mid-infrared spectroscopy (MIR) analysis of n- $HA/ZnS/PEEK^{[23]}$ revealed the characteristic bands of vibrations of sulfur-oxygen bonding at approx. 1240 cm^{-1} (asymmetric O=S=O stretching) and 1035 cm^{-1} (symmetric O=S=O stretching) in the spectrum, which did not appear in pure, non-sulfonated PEEK spectrum. Furthermore, the significant increase



Fig. 4—Current density variation for the EPD of the ZnS + PEEK (*a*) and HA (*b*) layers. Macroscopic images of as-deposited ZnS + PEEK coatings were also shown for the corresponding voltages in (a).



Fig. 5—Deposition yield (a) and deposition rate (b) of the ZnS + PEEK and HA layer on the Zr–2.5Nb alloy in relation to the time of deposition at a stable deposition voltage of 90 V.

in the intensity of the bands at 684, 1035, 1112 and 1243 cm⁻¹ associated with vibrations of the S–O bonds was additionally observed. Similarly, Moskalewicz *et al.*^[48] showed sulfonation of MoS₂/PEEK coatings at temperature of 390 °C, which is much lower than the thermal decomposition temperature of MoS₂ of about 650 °C.^[51] MIR analysis revealed the appearance the band at 1224 cm⁻¹, characteristic of the stretching vibrations of S = O, as well as the splitting of the band at around 1500 cm⁻¹ characteristic for aromatic C–C bonds, which is related to the appearance of the sulfur substitutions. In both cases of PEEK coatings containing ZnS and MoS₂, XRD patterns revealed an amorphous PEEK structure, which is not observed in pure

PEEK coatings or composite PEEK coatings^[35,38,52,53] without sulfides heat-treated under the same or similar conditions. This result also indicates sulfonation. Thus, the two-layered n-HA/PEEK + ZnS substrates were subjected to the same treatment.

The scratch resistance of the coating and the adhesion strength were investigated. First, the adhesion of the ZnS + PEEK coating to the Zr-2.5Nb alloy substrates was investigated. Unfortunately, the ZnS + PEEK coating achieved the worst class of adhesion (0B) to the asreceived alloy substrate graded with 600-grit sandpaper. The ZnS + PEEK layers, despite their homogeneity, were in some cases completely detached, starting from the upper edge, without being damaged. The upper area



Fig. 6—XRD patterns of ZnS + PEEK coated alloy heated at 380 °C (*a*) showing a semi-crystalline PEEK structure and heated at 450 °C (*b*) showing an amorphous PEEK structure.

of the layer on the sample was the main site of detachment due to the smaller thickness caused by sedimentation of the suspension during EPD. Thus, to enhance the adhesion strength of the layer to the surface of the substrate, it has undergone different thermal and chemical treatments. Thermal treatment was carried out to create an oxide layer on the alloy substrates. After thermal treatment of the alloy, the adhesion of ZnS + PEEK was not improved. Therefore, a chemical treatment of the substrate was applied. The ZnS + PEEK layer deposited on the chemically treated Zr-2.5Nb substrates exhibited a high class of adhesion (4B) (Figures 7(a) and (b)). Slight delamination of the coating occurred only near the pores in the path of the cut (Figure 7(a)). Finally, multicomponent Cu/HA/ZnS + PEEK coatings did not detach from the chemically treated substrate and exhibited the same high adhesion class (4B).

The micro-scratch test was carried out to investigate the mechanism of damage by scratching and to extend the coating adhesion analysis. The scratch results provide quantitative information on the coating adhesion to the alloy substrate. The critical load that causes characteristic coating failure is determined in the scratch test. At a critical load of L_{c1} , the first cohesive cracks emerge in the scratch track, L_{c2} causes the first adhesion deterioration with minor disclosure of the substrate, and L_{c3} is the load that causes massive delamination, with the thoroughly exposed area. The increase in the load transmitted by the stylus generates an increase in interfacial shear stress between the mobile and irregular surfaces of the coating. In addition, tensile stresses and pile-ups of the coating material occur at the edges of the scratch track.

It should be mentioned that the ZnS + PEEK base layers were much more resistant to scratch than previously reported multicomponent n-HA/ZnS/S-PEEK coatings.^[23] In the ZnS + PEEK layers, only cohesive cracks were found under the load of $L_{c1} = 23$ N and up to a load of 30 N no adhesive failures were observed (Figure 8). In contrast, in the multicomponent coatings, cohesive cracks appeared under the load L_{c1} of 16 N and the disclosure of the substrate under L_{c2} of 27 N. The difference in scratch resistance may be caused by differences in the microstructure of the coatings and the geometrical surface structure.

Electrophoretically deposited multilayered coatings contained numerous visible HA agglomerates and separate HA nanoparticles selectively embedded in the S-PEEK matrix, which formed a uniform solid matrix of the 1st layer (Figure 9). Thus, heat treatment caused a partial immersion of the HA in the PEEK matrix, which



Fig. 7—The surface of the ZnS + PEEK base coating on the chemically treated Zr-2.5Nb alloy after tape test, stereoscopic microscope image (*a*) and magnified SEM image of the cuts (*b*).



Fig. 8—SEM image of the ZnS + PEEK coating on the Zr-2.5Nb alloy after scratch test and the table with critical load determined during the test. Cohesive cracks were marked with arrow, SEM.

contributed to the high adhesion of the 2nd layer to the 1st one.

The as-deposited ZnS + PEEK layer thickness was in the range of 75 to 100 μ m. After deposition of HA, the thickness of the as-deposited double layered coatings increased to 85 to 190 μ m, reaching a thickness of about 120 μ m in the most parts of the coating. After heat treatment, the final thickness of the two-layered coating



Fig. 9—Surface morphology of the HA/ZnS + S-PEEK coating after heating at 450 °C for 30 min and cooling with the furnace, SEM.

was mostly in the range of 80 to 110 μ m, due to the filling of pores and cracks in the coating, and the melting of the polymer. Despite this, there were fragments of much greater thickness in the coating, reaching up to about 180 μ m, especially at the lower edge of the coating (Figure 10). SEM analysis of the cross-section (Figure 10) of the hybrid Cu/HA/ZnS + PEEK coating indicates that HA during the heat treatment was



Fig. 10—The cross-section of the Cu/HA/ZnS + PEEK coating, SEM. The yellow areola-labeled HA agglomerates marked were torn from the coating surface during the cutting and grinding of the sample (Color figure online).

submerged at different depths in the coating. All components formed a dense and homogeneous coating. HA agglomerates were found on the surface and indepth of the coating.

As a result of PLD with evenly distributed shadow masking, Cu "islands" were obtained on the surface of heat-treated multilayers (Figure 11). The HA was distributed non-uniformly on the surface of the coating. The ZnS distribution also varied on the coating surface. Such a distribution of components on the coating surface potentially allows for simultaneous antibacterial (Cu, ZnS) and bioactive (HA + S-PEEK) effects.

Moreover, the coating microstructure was examined by TEM on cross-section (Figures 12 and 13). The selective Cu layer at the top of the coating was from 200 to 500 nm thick. It was continuous, mostly uniform, with limited protrusions. No delamination was observed in the investigated area. The HA agglomerates were deeply inserted in the amorphous sulfonated PEEK matrix, reaching from the coating surface up to the alloy substrate. The agglomerates were shaped in various ways as submerged elongated "waves" and irregular particles with ECD from 50 nm to 8 µm. The differential location of the HA agglomerates resulted from the embedment of heavy ceramics in the soft polymer matrix during thermal treatment. Sporadically, ZnS particles were present in the PEEK matrix or in the HA agglomerates.

No closed porosity was observed on the cross-section of the coating. The element distribution images confirmed the presence of Cu in the outer "islands" layer, Ca and P in the HA, as well as Zn in the ZnS particles (Figures 11 and 13).

The roughness of the ZnS + PEEK, HA/ZnS + PEEKand Cu/HA/ZnS + PEEK layers was measured for particular layers. The ZnS + PEEK layer had the lowest roughness of the average arithmetical mean deviation (R_a) of $0.41\pm0.01 \ \mu\text{m}$, root mean square roughness (R_q) of $0.53\pm0.01 \ \mu\text{m}$ and the maximum peak to valley height (R_t) of $6.9\pm0.3 \ \mu\text{m}$. The HA/ZnS + PEEK multilayer had higher roughness, values of $R_a = 4.74\pm0.07 \ \mu\text{m}$, $R_q = 5.94\pm0.10 \ \mu\text{m}$ and $R_t = 49.2\pm7.6 \ \mu\text{m}$, due to the presence of HA agglomerates on the layer surface (Figures 10, 11, 13 and 14).

The thin Cu layer did not have a significant impact on the surface roughness of the multilayered coating. Representative images of the surface of the 1st ZnS + PEEK layer, the 2nd HA layer on the top of ZnS + PEEK layer and the final multilayered coating are shown in Figures 14(a) through (c). This relatively high surface roughness of the multilayered coating may be important due to the potentially better adhesion of bone cells. It is known,^[54,55] that high roughness and surface area stimulate the formation of the extracellular matrix.

The surface properties, wetting angle (WA) and interfacial free energy (IFE) of the developed materials were investigated and their values are present in Table I. During our previous study^[23] the WA and IFE for the Zr-2.5Nb substrate and the PEEK coating without additional components were characterized. The WA for the water of Zr-2.5Nb (53±8 deg) was lower in comparison to the PEEK coated alloy $(71.1 \pm 9.0 \text{ deg})$. The IFE of the alloy was marginally higher (53.6 ± 6.0) mN/m) than that of the PEEK $(51.3 \pm 4.1 \text{ mN/m})$ coating, these values were higher than for each layer of the three-layer coating. The WA and IFE of the 1st ZnS + PEEK layer of 70.7 ±4.5 deg and 40.8 ± 5.0 mN/ m, respectively, were comparable to those of the pure PEEK coating. Interestingly, both multilayer coatings, with and without Cu, exhibited mild hydrophobic WA at a level above 90 deg, with the highest WA of $109.7\pm$ 6.6 deg for Cu/HA/ZnS + S-PEEK coatings with IFE of 34.8 ± 1.1 mN/m. Although selective deposition of Cu did not have a considerable impact on surface roughness, it influenced the WA of the multilayered coating, increasing its hydrophobicity. It is well known that copper oxides form at a rapid rate when exposed to ambient air and that the oxide layer is not self-protective for further oxidation.^[56,57] Generally, copper oxides are also considered hydrophilic,^[58,59] but after exposure to ambient air, they become hydrophobic over time. This phenomenon was explained by Shirazy et al.^[60] They proved that volatile organic compounds in the air were responsible for the decrease in the hydrophilic properties of copper surfaces of various types. Similarly, Yin *et al.*^[61] studied the same dependence with the loss of hydrophilicity of TiO₂ in air.

In our study, the deposition of the Cu layer on HA/ZnS + PEEK coatings by PLD was performed in a vacuum, but the multilayered samples produced were not stored in a protective environment. Therefore, the potential contamination of volatile organic compounds



Fig. 11—Elements distribution on the Cu/n-HA/ZnS + S-PEEK coating surface, SEM–EDS.

may be responsible for the loss of hydrophilicity. Although the addition of HA could potentially lower WA due to an increase in the hydrophilic hydroxyl groups characteristic of HA on the surface of the composite,^[62,63] it was not observed in the investigated coatings. High WA indicates hydrophobicity of the coating, similar to HA/PEEK coatings electrophoretically deposited by Bastan et al.^[64] Although moderate hydrophilicity is preferred in cell adhesion studies.^[65–67] the results of the research vary. Hydrophilic cells are commonly approved to adhere to hydrophilic surfaces, whereas hydrophobic cells adhere to hydrophobic surfaces.^[68] Mild hydrophobicity may not adversely affect cell adsorption, because of the thermodynamic preference for protein adsorption from aqueous solutions.^[66] The surface of the coating has a significant influence on its wettability. In general, high hydrophobicity combined with a high surface area and high roughness of the coatings results in primal cellular adhesion.^[69]

Hardness (H_{IT}) and modulus of elasticity (E_{IT}) of the base 1st layer of ZnS + PEEK mainly responsible for the mechanical properties of the multilayered coating were investigated using of instrumented indentation under different loads (P_{max}) equal to 100, 200, 400 and 1000 mN. Only data acquired for 100 mN were analyzed because the standardized penetration depth of 10 pct of the coating thickness was not achieved at this load. Exceeding this depth causes disturbance of the results related to the interaction between the coating and alloy properties. The hardness value obtained was 0.21 ± 0.02 GPa and the modulus of elasticity was 3.7 ± 0.2 GPa. The hardness of the ZnS + PEEK coatings was marginally higher than that of the pure amorphous PEEK coating $(0.19\pm0.01$ GPa). Although, the Young modulus was lower than that of the amorphous PEEK coating (4.50 \pm 0.20 GPa) reported by Kruk *et al.*^[70]

The hybrid technology developed in this work may be used to obtain coatings with controlled bioactive and antibacterial properties. By developing Cu "islands", the coating can obtain an initial potential antibacterial response against the formation of bacterial microfilm, especially in the early stage of implantation. Moreover, the antimicrobial activity of Cu can be enhanced by ZnS particles. However, due to selective PLD, the contact of bioactive HA with bone is not limited. Further optimization of the antibacterial and bioactive phases on the top of the coatings, as well as advanced antibacterial and bioactive studies, are necessary.



Fig. 12—Microstructure of the Cu/HA/ZnS+PEEK coating on the cross-section, TEM.

IV. CONCLUSIONS

- 1. Hybrid technology involving EPD, heat treatment and PLD shadow masking allowed to obtain multilayered coatings on Zr–2.5Nb alloy substrates. The first ZnS + PEEK and the second HA layers were developed by the EPD at a constant voltage of 90 V during 15 seconds and at a voltage of 90 V during 30 seconds, respectively. The third outer selective Cu layer was deposited by PLD with the use of a special mask.
- 2. Heat treatment caused the transformation of the PEEK from particles into a continuous phase, in which ZnS particles were embedded. HA nanoparticles were selectively distributed on the multilayer coating surface and in the PEEK matrix of the 1st layer. The sulfonation of the PEEK occurred as a result of heating at 450 °C and slow cooling with the furnace. The PLD process led to the selective deposition of evenly distributed Cu "islands" on the coating surface. The obtained multilayer coating was characterized by high surface roughness and wettability in the hydrophobic range.



Fig. 13—Microstructure of the Cu/HA/ZnS + PEEK multilayer coating (HAADF-STEM image) and EDS element distribution images.

3. Conditions of surface preparation of the substrates have an important influence on the adhesion strength of the coatings. The ZnS + PEEK base layer showed very low adhesion (0B) to the untreated substrate. Chemical treatment of the Zr-2.5Nb substrate significantly increased the adhesion class (4B) and the scratch resistance of the coating. As a result of chemical treatment, multilayer coatings were characterized by high adhesion strength.

4. The hardness of the ZnS + PEEK base layer was slightly higher and the Young modulus was somewhat lower than that of the unfilled, amorphous PEEK coating and read the value of 0.21 ± 0.02 and 3.7 ± 0.2 GPa, respectively.



Fig. 14—3D images of the surface topography of the ZnS + PEEK layer (a) and the HA/ZnS + PEEK multilayer (b) after heat treatment at 450 °C and the final Cu/HA/ZnS + S-PEEK coating (c), optical profilometry.

 Table I.
 Water and Diiodomethane Wettability Angle and Interfacial Free Energy of the ZnS + PEEK, n-HA/ZnS + PEEK and Cu/n-HA/ZnS + S-PEEK Coatings

Material	WA (Deg)		IFE (mN/m)	
	H ₂ O	CH ₂ I ₂	Polar	Disperse
ZnS + PEEK layer	70.7 ± 4.5	56.2 ± 4.2	40.8±5.0	
			10 ± 2.5	30.8 ± 2.4
HA/ZnS + PEEK multilayer coating	93.8 ± 3.2	65.5 ± 1.6	27.6 ± 1.7	
			2.1 ± 0.9	25.4 ± 0.9
Cu/HA/ZnS + PEEK multilayer coating	109.7 ± 6.6	49.5 ± 1.1	34.8	3 ± 1.1
			0.5 ± 0.2	34.5 ± 0.6

ACKNOWLEDGMENTS

The study was supported by AGH-UST (project no. 16.16.110.663). The authors appreciate the valuable contribution of Dr M. Gajewska to TEM investigation, Dr A. Fioek for help with SEM investigation, and Prof. M. Sitarz (AGH University of Science and Technology) for help with wettability investigation.

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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