Development of Microstructure and Properties of Multicomponent MoS₂/HA/PEEK Coatings on a Titanium Alloy *Via* Electrophoretic Deposition and Heat Treatment

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In this study, molybdenum disulfide nanosheets, bioactive hydroxyapatite particles of two types in various amounts, and PEEK 704 microparticles were electrophoretically co-deposited to fabricate multicomponent coatings on Ti-13Nb-13Zr alloy substrates. A mixture of pure ethanol and cationic chitosan polyelectrolyte was used as a dispersion medium. The kinetics and mechanism of deposition were investigated. The kinetics depended significantly on the suspension's chemical composition and the voltage used during EPD. Cationic chitosan provided the steric stabilization of the suspension and enabled cathodic co-deposition of all coating components. Green macroscopically homogeneous coatings were subsequently heat treated. The treatment densified the coatings and caused the formation of a stable semi-crystalline PEEK matrix consisting of spherulites. The MoS₂ nanosheet packages, separate HA particles and their agglomerates were embedded in the coating matrix. After heat treatment, both types of coatings, differing in HA type, were characterized by excellent adhesion to the substrate and moderate scratch resistance. During surface topography investigation, it was found that coatings containing smaller HA nanoparticles had a slightly lower surface roughness. The coatings raised the corrosion resistance of the titanium alloy substrate in Ringer's solution. The possibility of the electrophoretic co-deposition of various ceramic and PEEK particles to develop multicomponent coatings, as well as their contribution to enhancing titanium alloy surface properties, represents an important input in further developing superior bioactive titanium implants.

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I. INTRODUCTION

AMONG all metallic materials, titanium alloys are widely used as implant materials due to their high strength to weight ratio, superior corrosion resistance and relatively low modulus of elasticity. One of the most promising alloys for medical applications is near- β Ti-13Nb-13Zr, which has a unique combination of

mechanical properties and electrochemical corrosion resistance.^[1] In contrast to $\alpha + \beta$ alloys, this alloy contains elements that exhibit a non-harmful reaction to human cells and has a Young's modulus about 30 pct lower.^[2] Unfortunately, it has been reported^[3,4] that titanium alloys, including Ti-13Nb-13Zr, exhibit poor bioactivity and osteointegration. One of the most promising ways of improving these properties is the deposition of bioactive coatings. Polyetheretherketone (PEEK) is a suitable polymer for biomedical coatings because of its chemical and dimensional stability, outstanding tribological properties, high strength and Young's modulus similar to that of cancellous bone.^[5-7] It is commonly used as a replacement for metallic, long-term, orthopedic implants due to its high performance and biocompatibility.^[8-11] It has been widely proven that PEEK-based coatings exhibit good adhesion to metallic substrates, which is the most critical issue in each application.^[12-15] In spite of its biocompatibility, the bioactivity of PEEK is rather poor.^[11-13,16-18] Among the various techniques

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available, two vital strategies are distinguished to induce PEEK bioactivity, surface modification or the preparation of composites. Improving PEEK's bioactivity through the preparation of composite coatings has been widely developed, using bioactive agents, such as hydroxyapatite (HA) in various forms,^[12,13,17,19–23] strontium containing HA,^[24] stearyltrimethylammonium chloride-modified HA,^[25] calcium silicate,^[26] β -tricalcium-phosphate^[27] and bioglass (BG).^[13,16,28,29] One of the most effective bioactive PEEK composite components is synthetically prepared HA. It is a primary non-organic bone ingredient.^[30] The effectiveness of HA's bone-bonding capability and enhanced implant stabilization has been clinically proven. The presence of synthetic HA causes natural HA accumulation and thus stimulation and acceleration of bone cell growth, which allows better implant and bone integration.^[31,32] The size and shape of HA particles are of great importance in the process of bone growth. It is known that nano-sized particles of HA enhance osseointegration through the mimicking of cells.^[17,22,33,34] Kalia *et al.*^[22] indicated that the shape of HA nanoparticles can influence the range of different parameters related to osteoblast viability and functionality. They reported that spherical HA particles have a greater osteogenic effect on osteoblasts, although oblong shaped HA particles cause a greater increase in intracellular Ca and P levels.

During osseointegration processes, it is very important to inhibit the development of the bacterial microfilm, which can cause inflammations that may be dangerous for patients' health or even be the reason for implant rejection.^[35] Among the most effective methods for preventing the development of bacterial microfilm on PEEK coatings is the use of antibacterial agents, such as sulfur,^[36–38] silver,^[29,39] copper,^[40] silicon nitride^[41] and chitosan.^[20,21] Another widely examined aseptic factor is MoS₂. Molybdenum disulfide is commonly used as a lubricant with a low coefficient of friction (COF) caused by a hexagonal S-Mo-S lattice structure.^[42] MoS₂ nanoparticles create an outstanding filler capability in composite coatings. Apart from excellent mechanical properties, recent studies^[42–44] confirm the high effectiveness of the MoS₂ antibacterial effect against gram-positive and gram-negative pathogens and their corresponding biofilms, which could be an alternative to the conventional small molecule-based antibiotics. One of the most intensively developing methods for producing PEEK-based coatings is electrophoretic deposition (EPD). EPD is a process in which charged particles suspended in a liquid move toward an electrode of opposite charge and then deposit on it to form a compact coating. It is characterized by a relatively short deposition time, carefully controlled deposition parameters and room temperature processing.^[45] A great advantage of EPD is the possibility to co-deposit polymer and ceramic particles in one process.^[12–15,20,22,28,29,42,46–59] This method is widely used for the deposition of composite PEEK-based coatings incorporating BG,^[16,28,29,54–56,59] BG and h-BN,^[58] HA,^[12,20,21,48] Si₃N₄,^[49,50] porous sol-gel glass,^[51] Al₂O₃^[15,52,57,60] and TiO₂.^[53] In our previous study,^[42]

we showed that MoS₂ nanosheets and PEEK microparticles can be electrophoretically deposited and heat treated. In the present work, multicomponent PEEK-based coatings containing bioactive HA nanoparticles and antibacterial MoS₂ nanosheets have been developed to induce dual antimicrobial and bioactive properties to the titanium alloy. Although bioactive (HA) and antibacterial (MoS₂) components in the PEEK matrix were previously studied,^[12,22,42] so far they have not been used simultaneously in coatings.

The aim of this study was to develop the electrophoretic co-deposition and heat treatment for the fabrication of multicomponent HA/MoS₂/PEEK704 coatings on the Ti-13Nb-13Zr titanium alloy substrates and characterize their microstructure, surface topography and selected properties. The influence of the shape and size of HA particles on the EPD as well as coating morphology and microstructure was also investigated. For understanding and strict control of the process itself, EPD kinetics and mechanisms were studied. To assess the quality of the coatings and their effect on alloy properties, the scratch resistance and adhesion of the coatings to substrates, micro-mechanical properties and electrochemical corrosion resistance in Ringer's solution were investigated.

II. EXPERIMENTAL

A. Substrate Material and Coating Components

Ti-13Nb-13Zr near- β titanium alloy substrates were delivered by Xi'an Saite Metal Materials Development Co., Ltd, China. The microstructure of the alloy was described in our previous study.^[9] It consists mainly of α' and sporadically α'' plates in β grains with a diameter of 10 to 80 μ m. Samples with a diameter of 27 mm and 4 mm thickness in the shape of disks were used for EPD. They were grounded with the use of 1200 grit sandpaper and subsequently washed in distilled water and technical ethanol. Four components were used for the deposition of multicomponent coatings. Polymer PEEK (VICOTE 704) powder was supplied by Victrex Europa GmbH, Germany. The melting temperature of the polymer is 343 °C and glass transition temperature is 143 °C, according to the manufacturer. MoS₂ nanosheets were delivered by Nanostructured & Amorphous Materials, Inc. (NanoAmor), USA. HA nanoparticles (NPs) with a mean particle size of 43 nm, according to the manufacturer, hereinafter referred to as HA1, were delivered by the Institute of High Pressure Physics of the Polish Academy of Sciences. HA in the form of powder with the mean particle size of 200 nm, according to the manufacturer, hereinafter referred to as HA2, was supplied by Sigma-Aldrich, Poland.

B. EPD and Heat Treatment Route

Suspensions containing 30 g/l of PEEK, 2, 6, 10, or 20 g/l of HA1 or HA2 and 0.4 g/l of MoS₂ powders in a dispersion phase composed of EtOH and 25 vol. pct chitosan solution were used for EPD. Medium

molecular weight chitosan with a degree of deacetylation of about 75 to 85 pct delivered by Sigma-Aldrich Poland was added to the suspension as a cationic dispersant. A chitosan solution (0.5 g/l) was prepared by mixing 1 vol. pct acetic acid, distilled water and magnetic stirring for 72 h at 300 rpm at room temperature (RT). Later in this work, this solution is named chitosan polyelectrolyte (CSp). Both MoS₂ and PEEK content were selected based on our previous study.^[42] The zeta potential of particles of three separate coating components in pure EtOH and EtOH with the addition of CSp was measured using a Zetasizer Nano ZS 90 of Malvern Instruments Ltd., (Malvern, UK) in a pH range from 3 to 12. In the case of the MoS₂ and HA1 components, measurements were conducted for the same concentrations as those used during coating deposition, while the PEEK suspensions were diluted 30 times to avoid multiple scattering. Each measurement was triplicated to average the results. To convert electrophoretic mobility values into zeta potential values, the Smoluchowski equation was used. The pH of the suspensions was lowered with hydrochloric acid (HCl) or increased with sodium hydroxide (NaOH). The pH values were determined by using an ELMETRON CPC-505 pH-meter (Poland).

EPD was carried out in a two-electrode cell with the use of a stainless steel (X2CrNiMo17-12-2) plate (dimensions of 30 mm × 15 mm × 1 mm) as the counter electrode and a titanium alloy substrate as the working electrode. The suspension was prepared gradually. Firstly, by dispersing PEEK and MoS₂ in a mixture of EtOH/CSp in an ultrasonic bath (Polsonic Sonic-3, Poland) at 50 Hz for 20 minutes. Then, by adding HA powder, magnetic stirring at 300 rpm for 10 minutes and dispersing for 10 minutes. Electrodes were immersed at a constant distance of 10 mm apart in the cell. Coatings were deposited at a constant voltage with the use of an EX752M Multi-mode PSU power supply, UK. Constant voltage in the range of 50 to 150 V with a 20 V change and a constant deposition time of 30 s were utilized, evaluating the coating homogeneity on the macro scale. A considerable area of the sample of about 5.3 cm² was exposed to deposition. During the EPD process, the influence of the applied voltage on current density was investigated using a Tektronix DMM 4040 multimeter, USA. Deposits were dried at RT and subsequently exposed to heat treatment in a laboratory oven (Carbolite Gero LHTO 4/30, UK). The heat treatment was performed at a temperature of 390 °C for 40 minutes with a heating rate of 4.5 °C/min, and cooled down at a rate of 2 °C/min. The heating temperature was determined based on differential scanning calorimetry (DSC) analysis and an experimental approach, assessing the morphology of the coatings. DSC analysis was conducted on pure PEEK and HA1/MoS₂/PEEK powders deposited from suspensions with the same composition as coatings with the use of a DSC 821e from Mettler Toledo, USA. Heating was carried out from 50 to 420 °C with a heating rate of 4.5 °C/min and an air flow of 60 cm³/min, for the powder mass of 8.23 mg and 6.41 mg, respectively.

C. Characterization of Microstructure and Surface Topography

Characterization of the coating components and coating microstructure was conducted by scanning and transmission electron microscopy (SEM, TEM). The SEM investigation was performed with an FEI Nova NanoSEM 450, the Netherlands. The TEM investigation was conducted using a JEOL JEM-2010 ARP microscope, Japan. The thin foils for TEM investigation were prepared by dipping a 300 mesh copper grid coated by carbon in the suspension of MoS₂ or HA in EtOH, respectively, and dried. The chemical composition was investigated by energy-dispersive X-ray spectroscopy (SEM-EDS, TEM-EDS) microanalysis. The phase composition was investigated by selected area electron diffraction (SAED) in TEM and X-ray diffractometry (XRD) in a Bragg-Brentano geometry using a Panalytical Empyrean DY1061 diffractometer, the Netherlands, with the use of Cu-K α radiation.

The surface topography of the coatings was examined using a Profilom 3D non-contact profilometer (Filmetrics, USA) with an accuracy of 0.1 nm. A comparison of the differences in the surface profiles between the samples was made based on the arithmetical mean height of the surface Sa (surface roughness parameter) and root mean square height (Sq).

D. Characterization of Selected Properties

The adhesion of the coatings to the underlying titanium alloy was examined by tape tests. The cross-cut tape test in accordance with ASTM D3359-17 was performed using an Elcometer 107. The tests were performed by making two cuts on the surfaces of the coating with a six-bladed knife with a spacing of 1 mm, at 90°. After that, patterns of the cuts were cleaned and stuck with standard-compliant tape, and finally turned off at 180°. The evaluation was performed by assessing the degree of coating detachment.

Scratch resistance of the coatings was investigated by a scratch test using a Rockwell C diamond stylus (indenter), 0.2 mm in radius, and a Micro-Combi Tester (MCT) of CSM Instruments (Switzerland). The tests were performed at a progressive load from 0.01 to 15 N on a scratch length of 5 mm with a constant velocity of the sample equal to 5 mm/min. During the tests, the critical loads (L_c) causing the characteristic coating damage were determined. These were the load of L_{c1} at which single cohesive cracks were observed, the load of L_{c2} that resulted in adhesive cracks and the L_{c3} load at which the coating was broken through due to delamination of the coating from the substrate. Three scratches were made for each coating and the paper presents representative results of this investigation. The hardness and elastic modulus were determined by the instrumented indentation method with the use of a Vickers diamond indenter. The indentation tests were performed at the peak loads of 50 and 100 mN, and the corresponding loading and unloading rates of 100 and 200 mN/min, respectively. The dwell time at a maximum load was 15 s. At least 10 measurements were made with

each load, changing the measurement place by several hundred micrometers each time to exclude the influence of the previous indentation. The paper presents the average value of the measurements. The coating thickness was measured with a contact profilometry method using the MCT. The diamond stylus scanned the sample over a 15 mm traversing length starting in the uncoated alloy area and finishing on the coated alloy surface.

The electrochemical studies of the samples were carried out using an Autolab PGSTAT302N potentiostat. Ringer's solution was used as the electrolyte for the corrosion study. The chemical composition of Ringer's solution was as follows: 8.6 g NaCl, 0.3 g KCl, 0.25 g CaCl_2 . The tests were carried out at 37 °C. Electrochemical measurements were performed for the pH equal to 7.4 and in deaerated solutions. The linear sweep voltamperometry curves were conducted at a scan rate of 1 mV/s in the potential range from -1.3 to $+2.2$ V. The measurements were performed using a classical three-electrode cell, where the working electrode was a titanium alloy. Potentials were measured vs. saturated calomel electrode (SCE) and the counter electrode was made of platinum wire.

III. RESULTS AND DISCUSSION

A. Deposition of Coatings

The coating components, MoS_2 and HA particles, used for EPD were investigated by TEM. It was found that the MoS_2 powder consisted of single-layer and multi-layer nanosheet packages with an equivalent circle diameter (ECD) in the range of 0.1 to 1.5 μm (Figure 1(a)). The SAED pattern revealed a hexagonal primitive (hp) structure (Figure 1(b)), while TEM-EDS microanalysis confirmed the presence of Mo and S in the particles (Figure 1(c)).

HA1 NPs exhibited oblong and round shapes with an average ECD up to 60 nm (Figure 2(a)). For oblong particles, the aspect ratio was from 1.34 to 2.50. HA2 showed a spherical morphology with two particle sizes: nanocrystalline with an ECD up to 100 nm and sub-microcrystalline with an ECD in the range 0.2 to 0.4 μm (Figures 3(a), (b)). It should be mentioned that the sub-microcrystalline particles occurred rarely. Analysis of SAED patterns indicated the occurrence of HA (hp) phase in both particle types (Figures 2(b) and 3(c)). The TEM-EDS microanalysis confirmed the presence of Ca, P and O in the particles. The typical EDS spectrum is shown in Figure 3(d). The Ca/P atomic ratio of both types of HA was determined to be around 2.1.

PEEK micro-particles were investigated elsewhere.^[50–52] They had a diameter in the range of 2 to 15 μm , globular and flattened irregular morphology as well as a mainly amorphous structure with a small amount of crystalline structure.

HA/ MoS_2 /PEEK coatings on Ti-13Nb-13Zr alloy substrates were developed based on an experimental investigation of the chemical composition of the suspension, as well as EPD parameters, voltage and time of deposition. EtOH was used as the main component of

Fig. 1—TEM image of MoS_2 nanosheets (a), SAED pattern taken from the area marked with a circle in Fig. 1(a) and its identification as MoS_2 (hp) (b) and TEM-EDS spectrum (c). The Cu in the EDS spectrum is from the TEM holder and copper grid.

the dispersant medium considering the hydrophobic properties of PEEK^[50] and electrolysis of water during the EPD process.^[51] In contrast to previous studies on EPD co-deposition of PEEK and HA^[12,22] or PEEK and BG,^[13,16,27,29] a cationic polyelectrolyte (CSp) was added to the suspensions. It is well known^[9,15,16,49,60] that PEEK particles in pure ethanol have a negative charge and they are deposited on the anode during EPD. The addition of CSp to ethanol changes the PEEK charge to positive, stabilizes the suspension, and enables the co-deposition of all components on the same cathodic electrode. The deposition mechanism of PEEK in the presence of chitosan was explained by Luo and Zhitomirsky.^[60] According to them, the formation of a coating is a result of the electrochemical decomposition of water at the cathode, which causes a local pH increase, as well as adsorption of protonated chitosan to PEEK particles and charge neutralization of the amino groups of chitosan at the cathode. In the present work,

Fig. 2—TEM image of HA1 NPs (a) and SAED pattern (b) taken from the area marked with a circle in (a) and its identification as HA (hp).

the suspensions containing 0.4 g/l of MoS₂, 30 g/l of PEEK, and different amounts of HA1 and HA2 of 2, 6, 10, or 20 g/l, were added to the EtOH/CSp solution with a volumetric ratio of 75/25.

Based on zeta potential measurement as well as SEM and TEM studies, the co-deposition mechanism of HA, MoS₂, and PEEK particles was proposed. According to a previous study,^[42] chitosan prevents the sedimentation of large PEEK particles in the suspension. The zeta potential of all coating components in pure EtOH and EtOH with the addition of 25 pct volume CSp was investigated. The zeta potential of individual components, *e.g.* MoS₂, HA1 and PEEK, in pure EtOH depended on the type of particles, and thus it had negative values for MoS₂, positive values for HA, as well as positive values for PEEK below pH 5.5 and negative ones above this value (Figure 4(a)). As shown in Figure 4(b), the inclusion of CSp stabilized the suspension and changed the zeta potential of MoS₂ from negative to positive values up to 9.0 pH. CSp increased the zeta potential of PEEK particles and shifted the isometric point from pH 5.5 to 7.5. In contrast, CSp decreased the zeta potential of HA for the whole investigated pH range. The zeta potential for suspensions with the addition of CSp exhibited a similar character for all components with positive values increasing up to a pH of about 4.5 and then declined continuously with an increase of the suspension pH (Figure 4(b)). The highest zeta potential for MoS₂ and

Fig. 3—SEM (a) and TEM (b) images of HA2 particles as well as SAED pattern (c) taken from the area marked with a circle in (b) and its identification as HA (hp.). The TEM-EDS spectrum taken from the area marked with a circle in (b) is shown in (d). Cu in the EDS spectrum is from the TEM holder and copper grid.

Fig. 4—Zeta potential of HA1 (1), PEEK (2) and MoS₂ (3) in pure EtOH (a) and EtOH with the addition of CSp (b) as a function of pH.

Fig. 5—TEM images of HA1 NPs with adsorbed CS clouds (a), MoS₂ nanosheet package with adsorbed CS (b), PEEK with adsorbed CS (c) and HA1 separate particles and their agglomerates adsorbed to the PEEK micro-particles (d) occurred in the suspensions used for the EPD of coatings.

PEEK in suspensions with the addition of CSp was found for a pH of about 4.5, while for HA it was for a pH of about 3.5. The pH of the suspensions containing HA1 and HA2 used for the EPD of coatings was about 5.02 and 5.22, respectively. Zeta potential values for

suspensions with these pH values for each component reach the value above 20 mV, which enables suspensions to be stable allowing efficient cathodic deposition, with limited agglomeration.^[61,62]

Typical TEM images of the interaction of cationic chitosan (CS) clouds (molecules and chains) with HA, MoS₂ and PEEK particles are shown in Figures 5(a) through (c), respectively. The CS clouds adsorb to HA NPs, MoS₂ nanosheets, and PEEK particle surfaces, providing steric stabilization of the suspension and enabling the co-deposition of ceramic and polymeric particles on the cathode (titanium alloy). However, considering the large differences in the particle diameter, electrostatic interaction was also observed between the MoS₂ packages and HA NPs (Figure 5(b)), as well as PEEK and HA NPs (Figure 5(d)). Similarly, Bastan *et al.*^[12] reported electrostatic interaction between the HA and the PEEK particles in suspensions due to the high specific surface energy of HA NPs. The scheme of the proposed complex mechanism of the electrophoretic co-deposition of all particles from the multicomponent suspension is shown in Figure 6.

Macroscopic images of coatings containing HA1 NPs and HA2 particles are shown in Figures 7 and 8, respectively. It was observed that the effect of voltage values on the macroscopic homogeneity of both coatings was very similar. Particle deposition was not observed at voltages lower than 50 V.

Coatings deposited at the voltage of 50 V and 70 V were relatively thin and inhomogeneous (Figures 7(a), (b) and 8(a), (b)). Coatings deposited at the voltage of 90 V and 110 V were dense and macroscopically homogeneous (Figures 7(c), (d) and 8(c), (d)). The voltage of 130 V and 150 V resulted in a gradual increase in the number and diameter of pores (Figures 7(e), (f) and 8(e), (f)) and caused exposition of the titanium alloy substrates. It was also observed that the higher content of HA in the suspension (above 2 g/l) caused a higher number of pores in both coating types. Therefore, the suspensions containing 0.4 g/l MoS₂, 2 g/l of HA and 30 g/l of PEEK were selected for the investigation of current density, deposition yield and deposition rate during EPD.

The deposition yield of the coating with HA1 NPs during the EPD process was lower than the coating with HA2 at 10 seconds, almost equal to the coating with HA2 at 20 seconds and then higher by 0.01 mg/cm² at the end of the EPD (30 seconds) (Figure 9(a)). The deposition rate of coatings with HA2 grew rapidly,

faster than that of the coatings with HA1 NPs and reached its maximum value in the first period of deposition (10 seconds), and then fell later in the process. The deposition rate of the coatings containing HA1 grew during the whole process. The most dynamic growth was in the first two stages of deposition, *e.g.* after 10 and 20 seconds. After 20 seconds, the deposition rate was close to the deposition rate of the coatings with HA2. In the third stage, the deposition rate of the coatings with HA1 was higher than the deposition rate of the coatings with HA2 particles (Figure 9(b)). Changes in the current density with deposition time of the coatings containing both types of HA at voltages of 30 V and 90 V were almost linear (Figure 10(a), (b)). In contrast, current density turbulence was observed during the first 5 seconds of both coating deposition at 150 V. Deposition at that voltage caused oscillation in the range from 575 to 620 mA/mm² for both coating types. These oscillations explain the macroscopic heterogeneity of coatings deposited at 150 V. The greatest changes were noted for the process at a voltage of 150 V. Interestingly, the most significant differences in the current density of the coatings were observed for deposition at 90 V. In the case of coatings containing HA1, the current density oscillated in the range from 100 to 110 mA/mm², while for those containing HA2 particles it was in the range of 300 to 320 mA/mm². During deposition at 30 V current changes were almost linear, of about 50 mA/mm² for coatings with HA1 and 100 mA for coatings with HA2. Current density changes were twofold and threefold the value for the coatings containing HA2 than for the coatings with HA1 during deposition at the voltage of 30 and 90 V, respectively. Such behavior may be a result of different thickness of the coatings. HA2/ MoS₂/PEEK coatings were much thicker than HA1/ MoS₂/PEEK coatings. The thickness of the coatings containing HA1 NPs was about 25 μ m and the coatings containing HA2 particles was about 30 to 35 μ m (see further parts of the work). It is well known that NPs tend to agglomerate. Differences in the deposition rate, yield and current density may indicate that the HA2 mixture of many spherical nanocrystalline and a few sub-microcrystalline particles and a lower tendency to agglomerate was deposited faster on the substrate surface, forming a thicker coating, thus reducing the current density effect. It is supposed that the coatings containing HA1 were deposited slower due to the higher agglomeration of smaller nanocrystalline particles. Moreover, larger HA particles cause a greater deposition rate and yield at the initial phase of deposition, because their lower quantity weighs more than the same quantity of smaller nanoparticles.

B. Microstructure and Surface Topography of Heat-Treated Coatings

Macroscopically homogeneous coatings with the addition of two different types of HA particles, deposited at the voltage of 90 V and time of 30 s were chosen for the post-EPD heat treatment and investigation of microstructure and properties. The DSC analysis was conducted to investigate the influence of HA and

Fig. 6—Schematic drawing of the electrophoretic co-deposition mechanism of the multicomponent HA/MoS₂/PEEK coatings.

Fig. 7—Macroscopic images of HA1/MoS₂/PEEK coatings on Ti-13Nb-13Zr alloy substrates deposited from the suspension containing 2 g/l HA1 at a voltage of 50 V (a), 70 V (b), 90 V (c), 110 V (d), 130 V (e) and 150 V (f) and a constant time of 30 s.

Fig. 8—Macroscopic images of HA2/MoS₂/PEEK coatings on Ti-13Nb-13Zr alloy substrates deposited from the suspension containing 2 g/l HA2, at a voltage of 50 V (a), 70 V (b), 90 V (c), 110 V (d), 130 V (e) and 150 V (f) and a constant time of 30 s.

Fig. 9—The changes in deposition yield (a) and deposition rate (b) with deposition time at a constant voltage of 90 V for suspensions with HA1 NPs and HA2 particles.

Fig. 10—The influence of deposition time on current density during the deposition of HA1/MoS₂/PEEK (a) and HA2/MoS₂/PEEK (b) coatings, with a constant voltage of 30 V, 90 V and 150 V during 30 s.

Fig. 11—DSC analysis of pure PEEK (1) and HA1/MoS₂/PEEK (2) powders.

MoS₂ particles on the thermal behavior of PEEK. Two types of powders were analyzed, pure PEEK and HA1/MoS₂/PEEK. The melting points of PEEK for both powders were similar, approx. 344 °C (Figure 11).

Based on the obtained results, the heating temperature of HA1/MoS₂/PEEK coatings should be about 344 °C, although our experiment demonstrated that even a heating temperature of 360 °C was not sufficient for obtaining good quality coatings. The morphology of the HA1/MoS₂/PEEK coating as-deposited from a suspension containing 2 g/l of HA and heated at 360 °C is shown in Figures 12(a), (b). Coatings heated at this temperature were macroscopically homogeneous on the whole coated area, but contained numerous microcracks and PEEK particles were only partially melted (Figures 12(b)). It was found that the coatings were homogeneous, dense and free from microcracks after

Fig. 12—Morphology of the as-deposited (a) and HA1/MoS₂/PEEK coatings heated at 360 °C (b) and 390 °C (c) as well as the HA2/MoS₂/PEEK coating heated at 390 °C (d). Coatings were deposited from suspensions containing 2 g/l of HA1 or HA2. SEM.

heating at a temperature of 380 °C and 390 °C. The difference between temperatures of densification of pure PEEK and HA1/MoS₂/PEEK coatings was probably caused by MoS₂ and HA1 nanoparticles surrounding PEEK particles as well as by degradation of chitosan during heating. Therefore, to stabilize and increase the repeatability of the process, it was decided to use the temperature of 390 °C during 40 minutes for the composite coating heating process and then cooling with a furnace. Coatings heated under these conditions were homogeneous and dense, without any discontinuities (Figure 12(c), (d)).

As a result of the heat treatment process of the alloy with coatings deposited from the suspension containing the lowest content of HA1 or HA2 (2 g/l), the PEEK morphology changed from a globular particles (Figure 12(a)) to a solid matrix (Figures 12(b) through (d)). PEEK spherulites, with ECD in the range of 4 to 13 μm, occurred in the coatings containing HA2 (Figure 12(d)).

Furthermore, after heat treatment on the surface of these coatings, several shallow pores occurred. In the coatings with HA1, the spherulites were hardly visible and they had a greater ECD by about 20 μm (Figure 12(c)). The surface morphology of these coatings was homogeneous. On the contrary, it was observed that the coatings with the higher HA addition of 6 g/l, 10 g/l and 20 g/l contained single, unmelted PEEK 704 particles surrounded by HA NPs adsorbed on their surface (Figure 13(a)). The presence of Ca and P was confirmed by EDS microanalysis (Figure 13(b)). It is believed that high ceramic content makes it even more difficult to obtain a continuous PEEK matrix. In addition, coatings deposited from suspensions with 6 g/l of both HA1 and HA2 contained micro-cracks (Figure 13(c)).

Due to the presence of unmelted particles in the coating matrix and the increased number of open pores on their surface, the coatings deposited from these suspensions were not subjected to further analysis.

XRD analysis of microscopically homogeneous coatings confirmed the presence of all components (HA, MoS₂, PEEK) in both coatings (Figure 14). Interestingly, the analysis indicated a relatively high volume of crystalline PEEK in the coatings. This result is surprising, because our previous work on MoS₂/PEEK coatings showed the amorphous structure of PEEK after a similar heat treatment route, thus indicating sulfur diffusion from MoS₂ to the coating.^[42] It is supposed that the presence of numerous HA NPs can reduce sulfur diffusion from MoS₂ nanosheets during heating and enables PEEK crystallization. The intensity of crystalline peaks of PEEK in coatings with HA1 was lower than in the coatings with HA2. This is in line with SEM observation of the coating surface, which showed a well-developed spherulitic morphology in the coatings with HA2 particles (Figure 12(d)).

Both HA1/MoS₂/PEEK and HA2/MoS₂/PEEK coatings showed a similar surface roughness (Figures 15(a), (b)) determined by the Sa parameter, which was $0.83 \pm 0.05 \mu\text{m}$ and $0.85 \pm 0.04 \mu\text{m}$, respectively. In the root mean square height, the trend was the same,

Fig. 13—SEM image of morphology of HA1/MoS₂/PEEK coatings deposited from suspensions with the addition of 10 g/l HA1 (a) and SEM-EDS spectrum taken from the area marked with a circle in (a), (b). (c) Microcracks of HA1/MoS₂/PEEK coatings deposited from suspensions with the addition of 6 g/l HA1, stereoscopic microscope. Ni in the EDS spectrum comes from the evaporation of the surface of the samples for SEM observation.

that is $S_q = 1.03 \pm 0.05 \mu\text{m}$ of the coatings with HA1 was slightly lower than $S_q = 1.11 \pm 0.04 \mu\text{m}$ of the coatings with HA2. Thus, both coatings deposited from the suspension containing 2 g/l of HA1 or HA2 had a similar surface geometrical structure, they were well

Fig. 14—XRD patterns of HA1/MoS₂/PEEK (a) and HA2/MoS₂/PEEK (b) coatings on the Ti-13Nb-13Zr alloy after heating at 390 °C for 40 min and cooling with an oven.

Fig. 15—3D images of the heat-treated HA1/MoS₂/PEEK (a) and HA2/MoS₂/PEEK (b) coating surface, optical profilometry.

Table I. Hardness (H_{IT}), Modulus of Elasticity (E_{IT}) and Penetration Depth (h_{max}) of the Coatings Measured with an Indenter Load (P_{max}) of 50 and 100 mN

Coating	P_{max} (mN)	H_{IT} (GPa)	E_{IT} (GPa)	h_{max} (nm)
HA1/MoS ₂ /PEEK	50	0.32 ± 0.02	5.7 ± 0.3	2910 ± 109
	100	0.39 ± 0.04	6.8 ± 0.7	3649 ± 173
HA2/MoS ₂ /PEEK	50	0.30 ± 0.05	5.4 ± 0.4	2905 ± 236
	100	0.33 ± 0.02	6.1 ± 0.3	4011 ± 184

developed, but uniform and without visible discontinuities.

C. Hardness and Elastic Modulus of the Coatings

Hardness (H_{IT}) and modulus of elasticity (E_{IT}) investigation was carried out using the instrumented indentation method with an indenter load (P_{max}) equal to 100 mN to eliminate the influence of coating surface roughness on the measurements. However, it turned out that, with a load of 100 mN, the penetration depth of the indenter (h_{max}) exceeded the limit of 0.1 of the coating thickness recommended in coating hardness measurement by the indentation method (Table I). For

this reason, indentation tests were performed with a lower load of 50 mN to minimize the influence of the substrate effect on the measured micromechanical parameters. The HA1/MoS₂/PEEK coating has a slightly higher hardness of 0.32 ± 0.02 GPa and elastic modulus of 5.7 ± 0.3 GPa compared to $H_{IT} = 0.30 \pm 0.05$ GPa and $E_{IT} = 5.4 \pm 0.4$ GPa for the HA2/MoS₂/PEEK coating with larger HA particles. Such differences were also found in the measurements with higher load, but the significantly higher H_{IT} and E_{IT} values are the effects of the metal substrate. The modulus of elasticity of both PEEK-based coatings doped with HA and MoS₂ particles was at a similar level to the HA/PEEK composite coatings developed through injection

molding by Bakar *et al.*^[23] for HA volumetric content in the range of 10 to 20 pct. It should be noted that the use of HA and MoS₂ fillers increased the hardness and elastic modulus of the HA/MoS₂/PEEK coatings compared to the previously investigated unfilled PEEK704, for which $H_{IT} = 0.26 \pm 0.03$ GPa and $E_{IT} = 4.7 \pm 0.3$ GPa.^[9]

D. Adhesion of the Coatings to the Substrate and Scratch Resistance

The tape tests conducted for the heat-treated coatings deposited from the suspension with the content of 2 g/l HA revealed that both coatings, regardless of the HA type used, exhibited high adhesion to the titanium alloy substrates. The excellent adhesion determined by the highest class 5B in accordance with ASTM D3359-17 was achieved for the coatings with HA1 NPs, while the class 4B was detected for the coatings with HA2 particles. The surface of the samples after tape tests are shown in Figure 16. Detailed investigation of the sample surfaces using SEM showed that the edges of cuts in the HA1/MoS₂/PEEK coatings were continuous without any cohesive cracks or coating delamination, both inside and outside the cuts (Figure 16(a)). In contrast, slight peeling on the outer edges of the cuts in the HA2/MoS₂/PEEK coatings was observed (Figure 16(b)).

The coating scratch resistance was investigated using a micro-scratch test, which allows a more precise analysis of the coating damage mechanism by scratching. Besides this, the critical load determined in the scratch test quantifies the degree of coating adherence to the substrate. In the conducted tests, the critical load at which the first, small cohesive cracks occurred in the

coating was defined as L_{c1} , the critical load causing cracks reaching the substrate with partial exposure of the substrate as L_{c2} , and the critical load L_{c3} , which resulted in complete failure of the coating induced by delamination. During the scratch test, the progressively loaded stylus causes an increase in the interfacial shear stress between the moving and deformed coating surface, as well as tensile stresses behind the stylus and in the coating pile-ups at the scratch edges.

The scratch test results, therefore, provide important information on the behavior of the coating-substrate system, which is in motion under high contact stress. When coatings are used as a barrier between the environment and the substrate, the tightness of the coating is important.^[63,64] Even a slight crack in the coating may favor penetration of the medium from the environment into the substrate. For this reason, the micro-scratch tests focused on the conditions that caused the formation of cohesive cracks, which may result in the loss of the tightness of the coating. However, small and shallow cohesive cracks in polymer coatings are not significant in the overall durability of the coating because their propagation is not so progressive as in the case of brittle ceramic coatings. Preliminary scratch tests with a progressive load of 0 to 30 N proved that both PEEK-based coatings were broken through when the load on the Rockwell indenter exceeded 12 N. For this reason, the main investigations were performed with the progressive load from 0 to 15 N. The failure mechanism of both coatings due to scratching was similar. The first single cohesive cracks of the HA1/MoS₂/PEEK and HA2/MoS₂/PEEK coatings were found at an L_{c1} load of 3.5 N and 5.4 N, respectively. At the load of L_{c1} , the initial arc cracks with the convexity in the direction of the indenter

Fig. 16—Stereoscopic microscope images of the surface of HA1/MoS₂/PEEK (a) and HA2/MoS₂/PEEK coatings (b) on the Ti-13Nb-13Zr alloy after tape tests. The enlarged details (SEM images) of the cuts marked with A and B are also presented.

Fig. 17—SEM images of scratch paths of HA1/MoS₂/PEEK (a, c, e) and HA2/MoS₂/PEEK (b, d, f) coatings in the places where the characteristic forms of failure occurred.

movement occurred but they were not deep and appeared in the central part of the scratch path (Figures 17(a), (b)). As the load increased, the number of cohesive cracks built up and there was also a clear deformation of the coating. Under the load of $L_{c2} = 8.5$

N for the coating with the addition of HA1 and at $L_{c2} = 10.2$ N for the coating with the addition of HA2, deep cracks reaching the substrate appeared (Figures 17(c) through (f)). These cracks curved inversely to the movement of the indenter, so they were a result of the

tensile stresses and caused local exposures of the substrate in the axis of the scratch path (directly under the indenter). Both coatings were destroyed as a result of delamination from the substrate with practically the same load, $L_{c3} = 13$ N (Figures 17(c) through (f)).

The scratch test results showed no beneficial effect of different HA1 and HA2 particles on the scratch resistance of the coatings. This behavior was caused by the tendency of HA NPs to agglomerate, and thus the lower degree of homogeneity of the coatings, which lowered their strength under scratch loading.

Moreover, composite HA/MoS₂/PEEK coatings exhibited a relatively small thickness, which in the case of polymer coatings does not favor their high scratch resistance due to the low load-bearing capacity of the relatively soft PEEK matrix. Browning *et al.*^[65] reported a flat increase in the scratch resistance of a polymer coating with an increase in its thickness. The HA2/MoS₂/PEEK704 coating showed a slightly better scratch resistance, confirmed by the L_{c1} and L_{c2} load values, which were higher than for the coating with the addition of HA1 NPs. However, the reason for this difference is probably the greater thickness (30 to 35 μm) of the coating with HA2 particles than that with HA1 NPs (25 μm). In addition, the HA2/MoS₂/PEEK coating exhibited a stronger structure, which was composed of more ordered spherulites. It should be mentioned that the investigated coatings are designed not for tribological applications (*e.g.* sliding bearings) but to enhance the bioactivity of titanium alloys in applications, in which the permanent adhesion of the implant with bone tissue is necessary. Micromovements usually occur in such applications and high shear stress caused by a frictional force is almost absent. Thus, the obtained scratch test results highlight the susceptibility to coating destruction due to a tangential movement at the simultaneous high contact stresses and indicate the need to increase the thickness of the coatings to improve scratch resistance if required by their application.

E. Corrosion Resistance

Figure 18a shows the evolution of the open circuit potential (OCP) for the uncoated as well as HA1/MoS₂/PEEK and HA2/MoS₂/PEEK coated alloy. The potential values of the HA1/MoS₂/PEEK and HA2/MoS₂/PEEK coatings at the beginning of the measurement equaled respectively -0.22 V and -0.35 V and changed in time, constantly increasing till reaching about 0.13 V and -0.16 V after approx. 1000 s. The OCP value of the uncoated alloy was stable in time and equaled -0.45 V. In the case of the coated alloy, a shift in the OCP value in the direction to more positive values may be attributed to the reduction of the driving force for the corrosion process.^[66,67] The difference in the OCP values of both coatings may be a result of their different morphology. The presence of larger HA2 particles caused the well-developed spherulitic morphology in the HA2/MoS₂/PEEK coating (Figure 12(d)), but also the presence of large pores on its surface (Figure 16(b)). In contrast, such large pores were not observed in the HA1/MoS₂/PEEK coating, while its adhesion to the titanium alloy substrate was higher than that of the HA2/MoS₂/PEEK coating, which contributed to a higher OCP value. Thus, the obtained results suggest that both coatings improved the corrosion behavior in comparison with the uncoated sample, while the improvement was slightly higher for the HA1/MoS₂/PEEK coated sample.

For a better comprehension of the corrosion behavior and properties of samples under investigation, potentiodynamic polarization experiments were performed (Figure 18(b)). Since registered LSV curves do not show linear regions, the interpretation based on Tafel extrapolation is not possible. Therefore, the estimations of corrosion rate can be performed by means of limiting the current density which passes through the passive film, consequently becoming a measure of the film protective performance.^[68,69] Compared with uncoated samples, coated ones exhibit a reduction in passive current density (i_p) values *i.e.* the values of this quantity

Fig. 18—Electrochemical measurements of the uncoated and HA/MoS₂/PEEK coated Ti-13Nb-13Zr alloy in Ringer's solution at 37 °C, (a) evolution of the corrosion potential vs. time and (b) polarization curves at 1 mV/s.

changed about four orders of magnitude—from 20 to $0.002 \mu\text{A}/\text{cm}^2$. A slight shift towards positive values was observed on corrosion potentials (E_{corr}) for both HA2/MoS₂/PEEK and HA1/MoS₂/PEEK coated samples when compared to the uncoated alloy, i.e. E_{corr} values increased from about -0.43 to -0.31 V and -0.29 V in the case of the latter coating, which is linked to improvement in the corrosion resistance of the coated alloys, as the coatings act as protective layers.

IV. CONCLUSIONS

In this study, the possibilities and effectiveness of obtaining multicomponent HA/MoS₂/PEEK coatings by electrophoretic co-deposition of PEEK 704 microparticles with various HA particles and MoS₂ nanosheets are discussed. The main conclusions are:

1. EPD and the heat treatment enabled the fabrication of dense multicomponent coatings on the Ti-13Nb-13Zr alloy substrates. The highest homogeneity of coatings was achieved for 2 g/l HA content in the suspension at 90 V during 30 s. Higher HA concentration in the suspension resulted in the formation of microcracks within the coatings.
2. EPD kinetics of both coatings was different. The deposition yield of the HA1/MoS₂/PEEK coatings compared to the HA2/MoS₂/PEEK ones was lower at 10 seconds, almost equal at 20 seconds and higher by $0.01 \text{ mg}/\text{cm}^2$ at the end of the process. The deposition rate of the HA2/MoS₂/PEEK coatings was faster than that of the HA1/MoS₂/PEEK coatings and reached its maximum value in the first period of the process.
3. The EPD mechanism of particle co-deposition was indicated. Both steric and electrostatic stabilization occurred in the suspensions used for EPD. The cationic chitosan polyelectrolyte stabilizes the suspension, while chitosan clouds adsorb to all suspension component particle enabling their cathodic deposition.
4. The microstructure of the heat-treated coatings consisted of HA separate particles and their agglomerates as well as MoS₂ nanosheets embedded in a continuous semi-crystalline PEEK matrix. HA1/MoS₂/PEEK coating thickness ($25 \mu\text{m}$) was thinner than HA2/MoS₂/PEEK (30 to $35 \mu\text{m}$) due to smaller HA NPs and differences in EPD kinetics of the coatings. PEEK spherulites occurred in both coatings. The surface topography of both coatings was similar. HA1/MoS₂/PEEK coatings exhibited slightly lower surface roughness.
5. Multicomponent coatings exhibited higher hardness and modulus of elasticity compared to the unfilled PEEK coating. Both coatings demonstrated high adhesion to the alloy substrates, but HA2/MoS₂/PEEK had a higher, excellent adhesion (class 5B) compared with HA1/MoS₂/PEEK (class 4B). Both coatings exhibited similar good scratch resistance despite their small thickness.

6. The uncoated alloy exhibited the worst corrosion resistance compared to the coated alloy. The HA2/MoS₂/PEEK coatings had slightly worse corrosion resistance compared to the HA1/MoS₂/PEEK coatings.

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