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Composite layers on titanium and Ti6Al4V alloy for medical applications

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Materials

ABSTRACT

Purpose: The paper presents the possibility of creating biomaterials through designing bioceramic composite layers on cpTi and Ti6Al4V alloy by hybrid method. $TiN+Ti_2N+\alpha Ti(N)$ and SiO_2-TiO_2 intermediate layer were produced by glow-discharge nitriding and sol-gel methods, respectively. Finally, hydroxyapatite nano-film deposited by electrophoresis.
Design/methodology/approach: The composite bioceramic systems were characterized from the standpoint of microstructure and morphology analysis of surface layers. The study was performed by X-ray diffraction technique, IR-fourier transform, SEM, AFM and in SBF (bioactivity). Wear resistance in environmental conditions (laboratory air) and in simulated body fluid (SBF) were carried out by pin-on-disc method.
Findings: The suggested innovative hybrid method allows the manufacture of the bioceramic composite layers with definite microstructure, phasic and chemical composition and surface topography. The intermediate layers are characterized by low thickness, good structural homogeneity, satisfying bonding with a metal substrate, whereas, external hydroxyapatite layer is very thin, homogenous, bioactive and durable.
Research limitations/implications: It seems necessary to conduct further investigation in the field of adhesion of composite systems and, particularly, biological study of capabilities of bone tissue and bacteriological behaviour in the environment of implant with studied layers.
Practical implications: The high layer quality, bioactivity and possibility of improving the mechanical properties of hydroxyapatite, it is advantageous to produce composite systems with $TiN+Ti_2N+\alpha Ti$ and SiO_2-TiO_2 intermediate layers.
Originality/value: The modification of the surface of metal substrate, produced by the hybrid method, may be an effective way to form a new generation of titanium biomaterials.
Keywords: Biomaterial; Hybrid method; Hydroxyapatite; Composite coatings; Titanium

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1. Introduction

Titanium and its alloys have been widely used in the manufacturing of dental and orthopaedic implants because of their superior mechanical property, low density, high corrosion resistance and excellent biocompatibility [1]. However, in recent years intensive development of medicine stimulates the demand for new titanium implant materials created by surface engineering [2-4]. One of the prospective and dynamic trends in this field are metal-bioceramic layers systems, which are particularly advantageous because of high physical and mechanical properties of titanium alloys with hydroxyapatite layer (HA), which has a positive effect on their biological activity [2,5,6]. On the other hand, HA layers have certain disadvantages, such as poor mechanical properties and insufficient bonding to the substrate materials [7,8]. Therefore, a great deal of research has been carried out to improve physical and chemical properties of the surface structure of metallic substrate and to obtain the suitable metal-ceramic bonding as well [2-4]. This goal may be reached through the deposition intermediate layers between metal substrate and final hydroxyapatite layer.

Various techniques have been used to produce bioceramic layers such as plasma spraying, sputtering, CVD, PVD, PDT, sol-gel and electrophoresis [2,5,6,9-12]. One of the new methods of implant surface modification are composites structures manufactured by hybrid method [12]. This method employs combining different surface treatments to obtain desired properties of elements. The composite bioceramic layers produced by hybrid method applying glow-discharge nitriding, sol-gel and electrophoresis are becoming increasingly important.

Essential advantages of this hybrid process, from the point of view of application on an implant, are the possibility of producing layers with specific structure, chemical and phase composition, surface morphology and good bonding with the substrate [2,5,7,12-14]. Needless to say, the layers produced in this method are characterized by satisfactory mechanical and chemical stability, high biocompatibility and corrosion resistance [9,15-19].

Moreover, particularly the process of manufacturing of sol-gel and electrophoretic coatings is economical and flexible, conducted in low temperatures with the possibility obtaining a wide ranges of thickness' and the prospect of formation of layers on substrate in complex shape or morphology [7,14,20].

The paper presents the possibility of creating new biomaterials through designing bioceramic composite layers on titanium and titanium alloy by hybrid method with the use of glow-discharge nitriding, sol–gel and electrophoresis methods.

2. Materials and methods

The commercial pure titanium cpTi (ASTM-grade 2) and Ti6Al4V alloy (ASTM-grade 5) with dimensions 15×10×2 mm were used as the metal substrate, then abraded with SiC paper (800), washed ultrasonically in acetone and ethyl alcohol.

The surface layer on metal substrate was produced by glow-discharge assisted by nitriding in pure nitrogen atmosphere at a the temperature of 1073 K (800ºC) and 4 hPa pressure for 3h. The process was carried out with the use of universal apparatus for different types of thermo-chemical treatment under glow discharge conditions (in Warsaw University of Technology).

Before layer depositing, all the samples were treated by acetone, ethyl absolute alcohol and HF to remove the impurities and fat. Next, the specimens with and without nitrided layer were twice precovered with titanium silica sol layer ($Si(OC_2H_5)_4$) and $Ti(OC_3H_7)_4$ using dip–withdrawing technique (dipping separated by drying in air). The layers were heat treated in argon atmosphere at 773 K (500ºC).

Finally, hydroxyapatite nano-film produced by electrophoresis method in ethanol HA (Chema-Elektromet Co., Poland and Aldrich Co.) suspension, with 10 - 30V tension in 10 – 30 s time, was repositioned and annealed at 1023 K (750 ºC). The thickness of the layer was controlled by selecting the depositing time and electric parameters of electrophoretic process. The deposition by sol-gel and electrophoresis methods was carried out in AGH University of Science and Technology.

The structure and morphology analysis of surface layers were performed by X-ray diffraction technique (Brucker D-8 Advance, X'Pert Philips: GID technique with special Soller slit and diffracted beam monochromator), IR-fourier transform BioRad (MIR-FTS60v spectrometer), scanning electron microscopes with EDS (Hitachi C-3500N, LEO 1430VP, Jeol JSM 5400), profilometer (Taylor Hobson Form Talysurf Series2) and atomic force microscope (Veeco MMN IIIA).

Wear resistance in environmental conditions (laboratory air) and in simulated body fluid (SBF) were carried out by pin-on-disc method (ASTM G 99-04). The WC ball with 0.5 mm diameter was used as a pin. The pin was pressed against the disk (the specimen) at the load of 50 g. The sliding distance was about 750 m. The wear test was evaluated from the cross-section profiles of the wear tracks measured by means of a Taylor-Hobson profilometer.

The initial study of bioactivity of composite layers was carried out in simulated body fluid environment (SBF) at 37^0C for 30 days. The chemical composition of SBF (according to Kokubo, in g/cm^3) is: 0.35 $NaHCO_3$, 0.07 Na_2SO_4, 0.3 KCl, 0.17 K_2HPO_4, 0.28 $CaCl_2$, 0.3 $MgCl_2{\cdot}6H_2O$, 8 NaCl, 6.05 $C_4H_{11}NO_3$.

3. Results and discussion

The typical topography of nitrided intermediate layer $TiN+Ti_2N+\alpha Ti(N)$, produced by glow-discharge nitriding method is shown in Figure 1. The layer is characterised by high compact, structural homogeneity and good bonding with a metal substrate.

The XRD analysis (see Fig. 2) confirmed the presence of compound three-zone surface layer consisting of δ - TiN, ε - Ti_2N and α-Ti(N) phase (interstitial solid solution). $TiN+Ti_2N+\alpha Ti(N)$ layer has a diffusive character. The surface microhardness of the layer was about 1750 HV0.05. The surface development of $TiN+Ti_2N+\alpha Ti(N)$ layer is non-uniform (see Fig. 1). The edge surface development slightly exceeded the centre surface development in the $TiN+Ti_2N+\alpha Ti(N)$ layer (centre R_a=0.432 µm, edge R_a=0.467 µm). This characteristic results from the possibilities provided by the method of glow-discharge nitriding. The technique allows producing the layer of specified roughness, if need be. It sems that this fact may have a positive impact on increasing the sol-gel and hydroxyapatite layers adhesion.

It is a well known fact that the nitriding of metal surface improves its mechanical properties [12,16,21]. Consequently, $TiN+Ti_2N+\alpha Ti(N)$ the layers on titanium and their alloys improve their resistance to friction wear, fatigue strength and corrosion resistance. Apart from that, $TiN+Ti_2N+\alpha Ti(N)$ layer can be characterized by biocompatibility, satisfactory cell growth and lack of cytotoxicity [16]. Its has also been established that the partial nitriding of Ti deposits in HA/Ti composite coatings improved the bond strength of the coatings on titanium substrate [22].

a)

b)

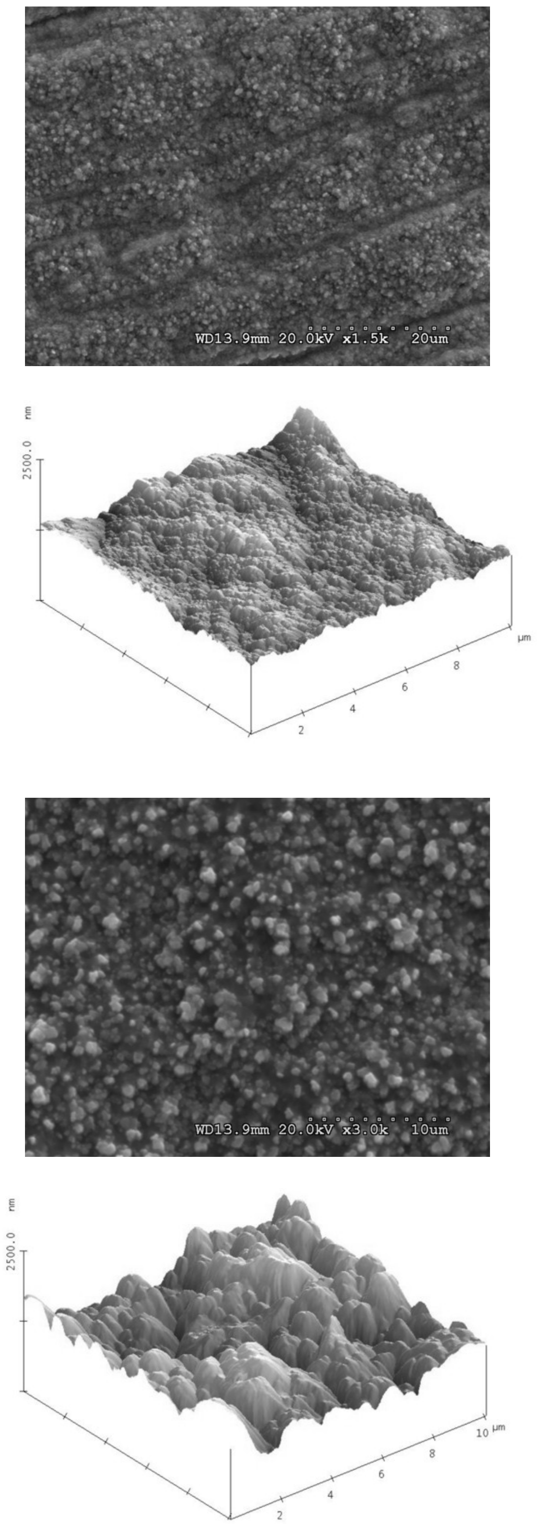


Fig. 1. SEM (up) and AFM (down) microphotograph of surface topography of nitrided layer on centre (a) and edge of specimen (b)

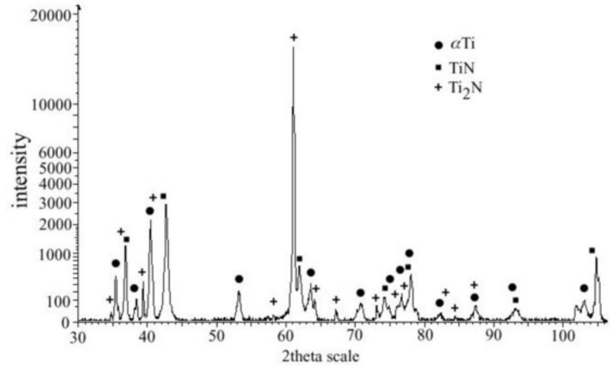


Fig. 2. X-ray diffraction pattern of nitrided intermediate layer on metal substrate, produced by glow-discharge nitriding process

Figure 3 presents the microstructure of SiO_2-TiO_2 on metal substrate with and without nitriding layer. From this figure it may be observed that the SiO_2-TiO_2 layer contains visible microcracks on its surface, formed during the heat treatment of layers. In the case of metal substrate with TiN+Ti_2N+αTi(N) intermediate layer, the structure of SiO_2-TiO_2 layers is more homogeneous and compact (see Fig. 3b) in comparison with the layers produced directly on titanium and Ti6Al4V alloy. During the analysis of surface topography of metal substate/TiN+Ti_2N+αTi(N)/SiO_2-TiO_2, smaller quantity of microcracks was observed on the centre of the specimen (intend smaller roughness of nitrided layer), rather than on edges (Figs. 3b,c). According to SEM observations, the adhesion of SiO_2-TiO_2 is satysfying.

The metals substrate/TiN+Ti_2N+αTi(N)/SiO_2-TiO_2/ hydroxyapatite composite system, produced by hybrid method, employing glow-discharge nitriding, sol–gel and electrophoresis methods are presented in Figure 4. Microscopic analysis of cross-sections suggests comparatively good structural homogenaty as well as acceptable adhesion of separate layers, particularly of the nitriding layer (thickness of about 4 μm). In the SiO_2-TiO_2 layer (thickness of about 3-6 μm) microcracks have been noticed, which, as I have already mentioned, are connected with the characteristics of these layers and their process of production. The SEM observation of HA layers is hindered due to its thinness (below 1 μm). It seems that bioceramic hydroxyapatite layer produced in this way is denser, smoother, homogenous, and has a satisfying bonding with the substrate. It also appears that it fills the present microcracks in the SiO_2-TiO_2 layer.

However, SEM observations (Fig. 5) showed local discontinuity (microcracks) in the central zone, while the greater presence of microcracks has been noticed near the borders. It may be observed that the quality of hydroxyapatite with TiN+Ti_2N+αTi(N) and SiO_2-TiO_2 intermediate layers is considerably higher than composite systems of only SiO_2-TiO_2.

The sol-gel intermediate layers are beneficial because of the possibility of producing controlled interactions between substrate materials and bioactive hydroxyapatite layers. TiO_2 has positive effect on the mechanical and biological properties of HA layers [23-25]. Moreover, they improve the adhesion of HA to the substrate [18,20,26]. The layer prepared by nanometer titanium oxide powders possesses the excellent biocompatibility [27]. On the other hand, SiO_2 and TiO_2 layer produced by sol-gel technique are able to stimulate apatite formation from SBF [28]. SiO_2-TiO_2 layer seems to have these properties simultaneously. Therefore, the SiO_2-TiO_2 intermediate layers reacting with metal substrate improve adhesion, preserving compatibility with HA layer and give a good compactness of whole composite layer as well (see Fig 5). The earlier studies show that SiO_2-TiO_2 used as intermediate layer between metal substrate and dental porcelain increased the bond strength [13,17].

a)

b)

c)

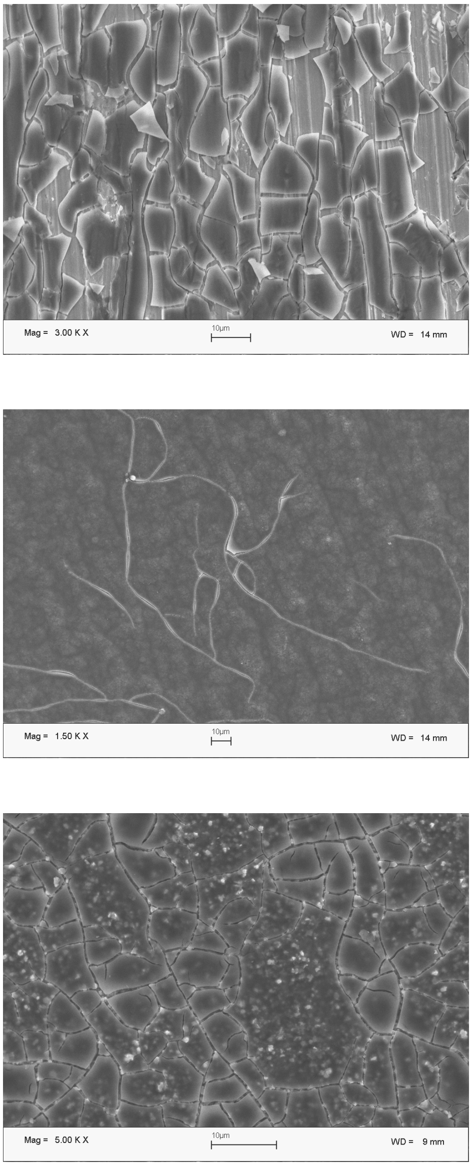


Fig. 3. SEM microphotograph of SiO_2-TiO_2 intermediate layers; (a) on metal substrate, (b) with TiN+Ti_2N+αTi(N) intermediate layer - centre of specimen, (c) with TiN+Ti_2N+αTi(N) – edge of specimen

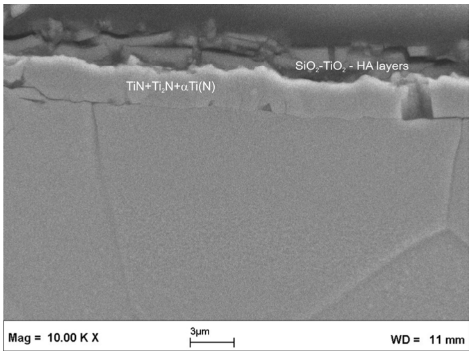


Fig. 4. SEM microphotograph of the cross-section of the metal substrate/TiN+Ti_2N+αTi(N)/SiO_2-TiO_2/hydroxyapatite composite system

a)

b)

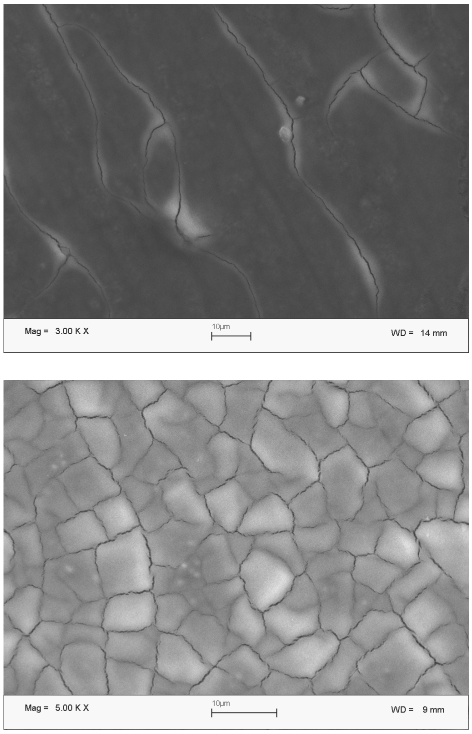


Fig. 5. Surface morphology of metal substrate/TiN+Ti_2N+αTi(N)/SiO_2-TiO_2/hydroxyapatite composite system; centre (a) and edge (b) of specimen

Numerous microcracks observed in the microstructure of SiO_2-TiO_2 and hydroxyapatite layers, may be attributed to the effect of high soaking temperature during the sol-gel and electrophoresis process (see Fig. 3). Guille´n et al. [29] suggests that the formation of microcracks in sol-gel layers is affected by the number of layers depositioned one on another and the thickness of each deposited layer. According to them, mechanical stresses are accumulated during the production of each layer followed by heat treatment. The cracking on SiO_2-TiO_2 and HA surface layers was observed probably due to mismatching the coefficient of thermal expansion between the coating and substrates (CTE of titanium amounts to only 60% of that HA). As Breme argues [1], due to the large difference in thermal expansion coefficients, tension stresses will occur, causing a decrease in the adhesion strength through cracking. The HA layer should be as thin as possible [1]. It has been found that the thicker the coating (HA), the greater the susceptibility to cracking. In our studies the homogenous and very thin HA layer were obtained (see Fig. 5) and the amount of cracks is smaller both in SiO_2-TiO_2 and HA, if the system includes the nitrided layer. It supports the theses that nitrided layers have a positive effect on the internal stress state within the layer.

On the other hand, Milella et al. [26], concluded that microcracks formed due to shrinkage, which occurred during thermal treatment, can become the points of ‘‘mechanical interlocking’’ to enhance osteintegration. Moreover, it is probable that the borders of cracks themselves act as a center of heterogeneous nucleation for the apatite, witch during its growth, tends to arrange inside the cracks, filling them completely [5]. Similar results in the case porous sol-gel layers were observed [30]. Besides, the increase of surface structure, which can enlarge the number of apatite nucleation sites, is a beneficial factor as well. Moreover, osteoblastic cells attach faster to rougher surface and they are able to migrate across rough surface [23]. Generally speaking, rough surfaces support bacterial adhesion to a larger extent, however, it is emphasized that this tendency depends more on the chemical composition of the layer than on its roughness [24].

It has also been proven that the oxidation layer is present in the interface between the material substrate-titanium and other deposited layers (e.g. hydroxyapatite), which decreases the bonding strengths of the coatings on these substrates. Because of established high affinity for oxygen to titanium, excessive oxide formation on the titanium surface has been observed in the increased temperatures [31-33]. The interfacial oxide layer can be porous, nonprotective, non-adherent, and unsuitable for layers bonding. Greatly lower crystallizing temperatures of the HA coating reduce the possibility of oxidization of metal substrate [8]. It can be assumed, that SiO_2-TiO_2 and particularly TiN+Ti_2N+$\alpha Ti(N)$ intermediate coatings show higher resistance to oxidation at elevated temperatures and constitute oxygen diffusion barrier against metal substrate during the heat treatment of intermediate layers and porcelain firing, causing the increase of the metal-porcelain bond strength.

The infrared spectroscopy studies show that the process of electrophoresis is very effective. We can compare the spectra of layers before and after HA deposition (Fig. 6a down and up).

All the bands characteristic for P-O bonds vibrations are present on the spectrum of HA covered sample. The results are more obvious after mathematic treatment of the spectra (BIO-RAD Win IR program, Arithmetic-substract function). The spectrum of mathematically substracted HA layer is almost identical with the spectrum of pure synthetic hydroxyapatite (Fig. 6b up and down). The only differences are in the sharpness of some bands (for example 633 or 1093 cm^{-1}) connected with lower crystallinity of obtained layer in comparison with synthetic phase. On the spectrum of HA layer we can observe very low intensive bands connected with the presences of carbonate (about 1450 and 1570 cm^{-1}) and organic (2850-2950 cm^{-1}) groups.

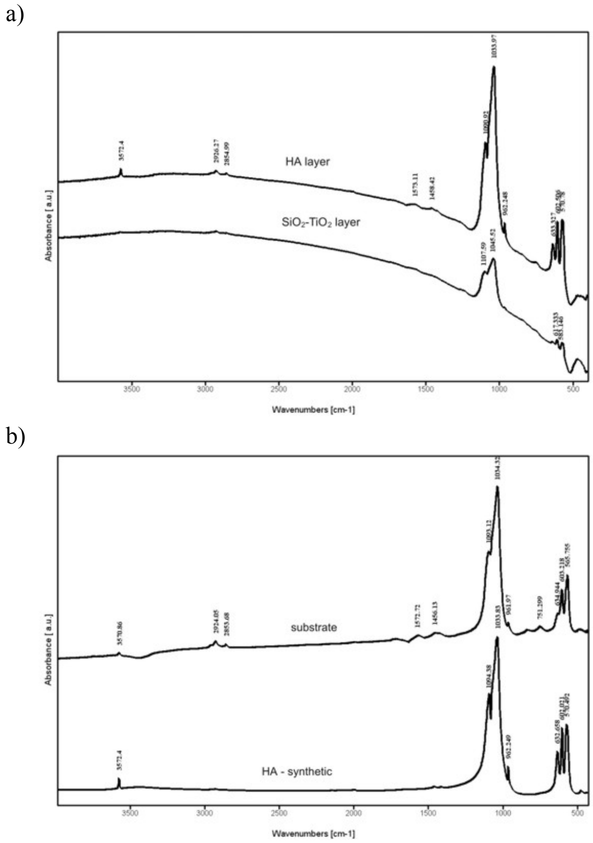


Fig. 6. FTIR spectra of HA layers: (a) before (down) and after (up) HA deposition, (b) the spectrum of mathematically substracted HA layer (up) and pure synthetic HA (down)

The XRD (GID method) of obtained HA layers showed their fine-crystallinity or even (partially) amorphous character - on the X-ray patterns we can not observe any peaks characteristic for phosphate or phosphor-silicate phase (only the peaks characteristic for metal base are observed). The GID method enables the observance of the peaks of a very low intensity, characteristic for HA phase (Fig. 7).

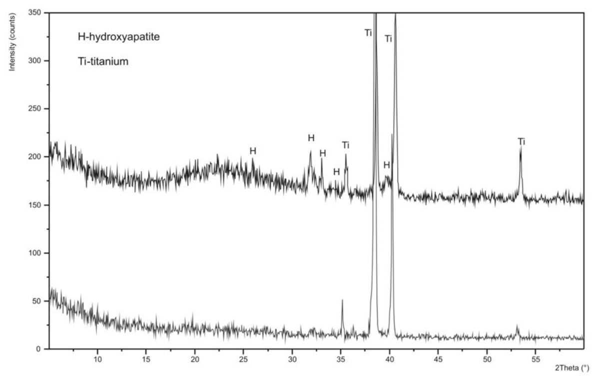


Fig. 7. X-ray patterns of hydroxyapatite layer (traditional XRD method-down and GID method-up)

Obtaining high crystallinity of HA showing low-dissolution rates and less resorption is believed to be advantageous [34]. HA coatings with higher crystallinity yielded higher rates of cell proliferation [35]. Some authors concluded that large amounts of amorphous phases in the layer may cause their excessive dissolution and, consequently, weakening and disintegration of the layer, frequently causing inflammatory responses in the tissues leading to the decrease of reliability and lifetime of an implant [34,36].

On the contrary, it has been reported that lower crystallinity hydroxapatite layer shows high bioactivity and may activate beneficial conditions for the attachment of cells and certain proteins. Their partial dissolution in initial stage may accelerate bonding o fan implant with the bone, leading to the stimulation of growth and adhesion bone tissue [34,36]. The increase of crystallinity of the layers, for example through thermal treatment, may cause substantial weakening of mechanical properties [34]. Therefore, the structure of hydroxapatite seems to be a compromise, which, I believe, has been reached in this study.

Results of wear resistance of bio-ceramic layers produced by hybrid method are listed in Table 1. The highest wear resistance were observed for structures with TiN layers and also for bio-ceramic layers, particularly in SBF environment (see Table 1).

Table 1.
Wear in the environmental conditions and in the SBF

	air [μm^2]	SBF [μm^2]
cpTi	4680	10951
cpTi/TiN	283	290
cpTi/SiO_2-TiO_2/HA	4109	257
cpTi/TiN/SiO_2-TiO_2/HA	117	288
Ti6Al4V	4283	5945
Ti6Al4V/TiN	112	80
Ti6Al4V/SiO_2-TiO_2/HA	3501	66
Ti6Al4V/TiN/SiO_2-TiO_2/HA	81	60

The substrates (titanium and titanium alloy) wore down considerably in the both study environments – the laboratory air and simulated body fluid. The difference in the wear resistance of bio-ceramic layers may be connected to microstructure, properties, surface topography, character of wear and influence of SBF environment.

The surface topography (wear tracks) of the studied materials after wear tests are shown in Figure 8. During the SEM analysis of wear tracks, shear of the highest peaks of roughness, micromachining and plastic deformations were observed [37]. The worn surface of the uncoated cpTi and Ti6Al4V alloy was characterized by typical features of adhesive and abrasive wear. The wear track is very narrow and shallow (see Fig. 8) after the tests in the SBF environment.

The preliminary comparative studies of bioactivity of composite layers in simulated body fluid environment indicated that growth of hydroxyapatite on specimen surface (Figs. 9a,b). From the point of view of potential bio-applications, the possibility of HA growth in the physiological environment is more significant that the fact of its presence on the surface of an implant. The bio-activity tests of the created composite structure signify not only that HA layer dissolves, but it stimulates the HA growth. It confirms obtaining expected bioactivity properties by composite layers.

a)
b)
c)
d)

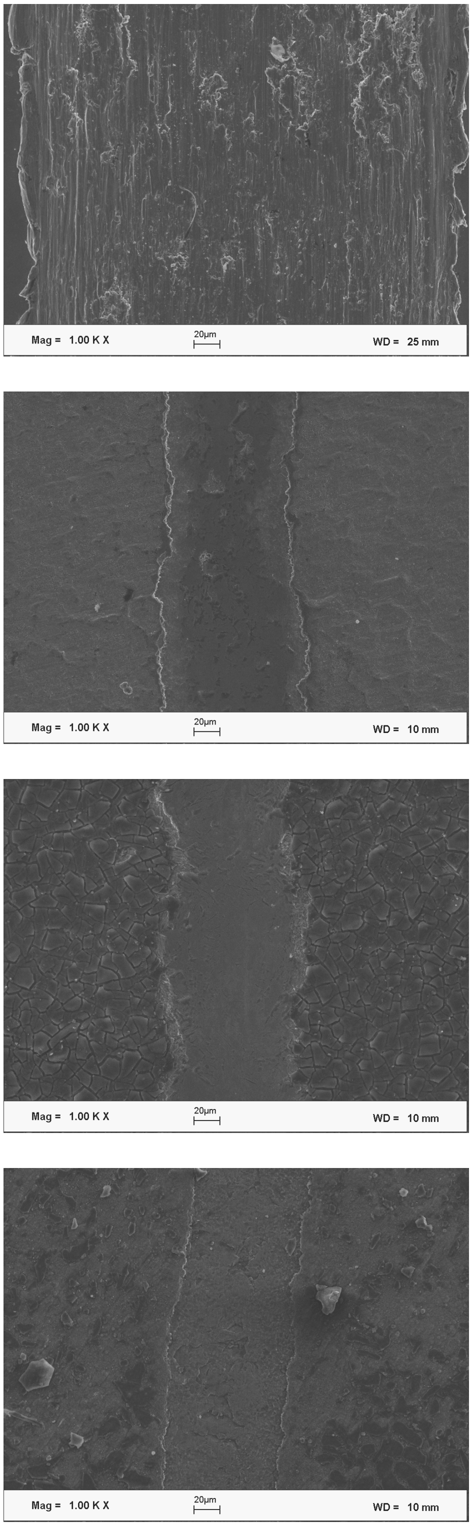
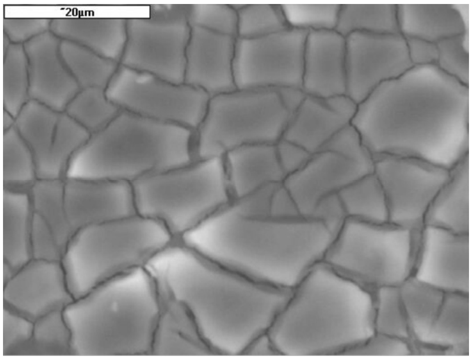


Fig. 8. The wear tracks after test in SBF: (a) cpTi, (b) cpTi/TiN, (c) cpTi/SiO_2-TiO_2/HA, (d) cpTi/TiN/SiO_2-TiO_2/HA

a)



b)

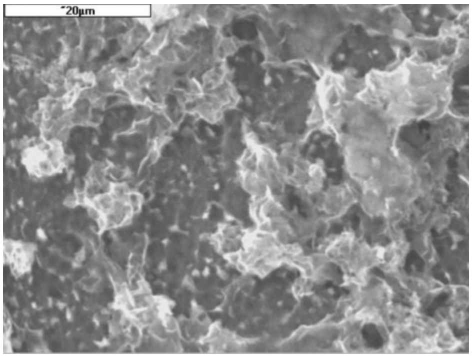


Fig. 9. SEM microphotograph of surface morphology of HA layer before and after soaking in SBF

It seems necessary to conduct further investigation in the field of adhesion of composite systems and, particularly, biological study of capabilities of bone tissue and bacteriological behaviour in the environment of implant with studied layers. That section should have a character of a scientific discussion, although in order to do that the separate section can be created and in the given one only the information about achieved results of researches can be included. In short papers you should rather limit yourself to a discussion.

4. Conclusions

The suggested innovative hybrid method: glow-discharge nitriding, sol-gel and electrophoresis allows the manufacture of the bioceramic composite layers with definite microstructure, phasic and chemical composition and surface topography. Individual physical and chemical properties of both $TiN+Ti_2N+\alpha Ti(N)$ and SiO_2-TiO_2 intermediate and bioceramic hydroxyapatite layers and the techniques of their production can play a significant role in designing functional properties of medical implants. The intermediate layers on titanium and Ti6Al4V alloy are characterized by low thickness, good structural homogeneity, satisfying bonding with a metal substrate, whereas, external hydroxyapatite layer is very thin, homogenous and, according to the SBF tests, bioactive and durable.

Taking into consideration high layer quality, wear resistance, bioactivity and possibility of improving the mechanical properties of hydroxyapatite, it is advantageous to produce composite systems with $TiN+Ti_2N+\alpha Ti$ and SiO_2-TiO_2 intermediate layers.

It is believed that the modification of the surface of metal substrate, produced by the hybrid method, may be an effective way to form a new generation of titanium biomaterials.

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