

Determination of Structural, Mechanical and Corrosion Properties of Titanium Alloy Covered by Thin Films Based on Graphene and Silicon Nitride*

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We report the comparative studies on structural, mechanical and corrosion properties of TiAlV/SiN, TiAlV/SiN/graphene and Ti/graphene/SiN coatings. The deposited silicon nitride thin film and silicon nitride/graphene coatings systems were crack free, exhibited good adherence to the substrate, no discontinuous of the thin films was observed and the surface morphology was homogeneous. The silicon nitride thin film deposited on graphene monolayer in graphene/silicon nitride coating system, was pilling off and had poor adhesion to the graphene surface. Graphene transferred on titanium alloy surface and silicon nitride thin film surface was a single layer without defects. The hardness of silicon nitride thin film was ca. 22.4 GPa, SiN/graphene coatings system was equal 23.0 GPa and graphene/SiN coatings system was equal 22.2 GPa, showing that graphene monolayer has no affect on surface hardness of silicon nitride thin film, but at the same time it causes the decrease in the electrochemical activity of the system. The best corrosion resistance has the sample Ti6Al4V coated with SiN/graphene coatings system. This sample retains the most stable mechanical and structural parameters during corrosion process. The SiN/graphene coatings system greatly improve the mechanical and corrosion properties of examined titanium alloy surface. [DOI: 10.1380/ejsnt.2015.289]

Keywords: Silicon nitride thin film; Nanoindentation; Electrochemical properties; Graphene; PECVD method

I. INTRODUCTION

In the last period we observe a significant increase in the world-wide production of castings from light metal alloys such as titanium. It is associated not only with an increase in the demand for lightweight structural components in the automotive, the aviation and the aerospace industry, but also with an increase in the interest from manufacturers of various household appliances, electronics, video cameras, mobile phones and others. Particularly rapid growth in the production of castings from titanium alloys is observed in Germany, Italy and the USA. Wide application of titanium and its alloys in various fields is due to their excellent mechanical properties *i.e.* small specific gravity, high yield strength and the modulus of elasticity that allow the transfer of heavy loads, excellent corrosion resistance and the biocompatibility [1]. The excellent corrosion resistance of titanium in various test solutions and physiological media is due to the formation of protective oxide-TiO₂ layer on its surface [2]. The oxides layers are barrier between the surrounding environment and the underlying metallic titanium, which inhibit the subsequent oxidation of metallic titanium across the metal-oxides barrier layer-solution interface [3].

Titanium and its alloys have many potential industrial applications, but their implementation is limited due to problems with unsatisfactory surface mechanical parameters, *i.e.* low hardness, low wear resistance and low corrosion resistance in hot, concentrated and low-pH solutions [4–8]. Therefore, many various surface treatment techniques are used, to improve titanium and its alloys mechanical properties. These methods include, burnishing and surface micro-shot peening and thermo-chemical treatment, in particular based on the PVD and CVD

methods [9–11].

One way to protect titanium alloy surface from corrosion and improve its surface mechanical properties is the application of ceramics coatings *i.e.* silicon nitride. It leads to the metal's insulation from environmental stress by the unbreakable, durable, elastic and at the same time wear resistance and harder than titanium alloy surface, oxide films [12]. Silicon nitride thin films are characterized by high density, low wear rates, good insulating properties, excellent Na⁺ resistance, relatively high fracture toughness, strength, high temperature corrosion resistance in oxidizing atmosphere and in sulphidizing-oxidizing atmosphere [13] and excellent biocompatibility [14–17]. They are excellent diffusion barrier against water and aggressive contaminants which may corrode titanium alloys [18]. Silicon nitride films can be deposited by low-pressure-chemical-vapor-deposition (LPCVD), plasma enhanced chemical vapour deposition (PECVD) or reactive radio frequency (r.f.) sputtering techniques. Unfortunately, their structural, mechanical and corrosion properties highly depend on technological process used during sample fabrication and processing [19–21]. Olofsson *et al.* in [19] used reactive r.f. sputtering to produce Si_xN_y coating that showed a potential for high wear resistance, but issues with coating defects and poor adhesion leading to flaking off of the coating were reported. Shi *et al.* in [20] also used different magnetron sputtering methods for fabricating Si_xN_y coating; r.f., direct current and unbalanced magnetron sputtering. However, adhesive properties of the coating were not reported.

Another way to improve titanium alloys surface properties can be the use of graphene as a protective layer. Studies have shown that a single graphene layer considerably increases the corrosion resistance of such systems as copper/graphene [22], nickel/graphene [23] and titanium alloy/graphene [24] and protects the surface of those metal from oxidation [24].

The purpose of this manuscript is to show that hybrid coating systems based on silicon nitride thin films

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and graphene monolayer can be used as a layer system for protection of titanium alloy surface against the corrosion process and improve its surface mechanical properties. In this work, surface, structural, mechanical and corrosion properties of two different hybrid systems *i.e.* SiN/graphene/Ti-Al-V and graphene/SiN/Ti-Al-V have been investigated and compared with pure titanium alloy and SiN/Ti-Al-V system.

II. MATERIALS AND METHODS

A. Experimental design

1. Specimen preparation

For the purpose of the experiment, three sets of titanium alloy Ti6Al4V (ASTM Grade 5, UNS R56400) (Table I) were prepared in the same manner. Before technological processes, the Ti alloy surfaces were polished using a grinding and polishing Stuers RotoPol 21 apparatus. The sample surface was polished to a “mirror image”. In the next stage, samples were cleaned in an acetone solution.

2. The silicon nitride thin films preparation

The amorphous silicon nitrides thin films were fabricated in Oxford Plasma Technology PlasmaLab 80 Plus System, which is a parallel plate PECVD (13.56 MHz) deposition system. The computer system allows predefining of the process parameter value and their control in real-time during the process. The films prepared by PECVD method have a lot of advantages, such as low deposition temperature, high growth rate, good uniformity and good adhesion to the substrate surface [25].

In order to achieve a range in composition of the SiN films, process parameters such as the deposition pressure, the gas flow rates of SiH₄ and NH₃, the deposition temperature and total gas flow rate were kept constant. Table II shows a summary of the parameters used for the deposition of SiN films in this study.

TABLE I. Composition of Ti6Al4V titanium alloy.

Components, wt. %						
C	Fe	N	O	Al	V	Ti
0.08	0.25	0.05	0.20	5.50–6.75	3.5–4.5	Bal.

TABLE II. Summary of the Si_xN_y process parameters.

RF Power [W]	120
Pressure [Torr]	0.8
SiH ₄ gas flow [ml/min]	150
NH ₃ gas flow [ml/min]	50
Temperature [°C]	350

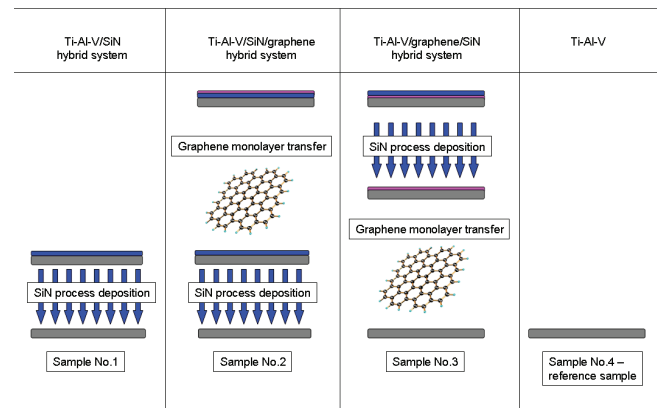


FIG. 1. Schematic procedure of the test samples preparation.

3. Graphene layer preparation

The graphene monolayers were grown on 18- μ m thick copper foil using chemical vapor deposition (CVD) technique. For this purpose a home-made CVD set based on Blue M Tube Furnace with 1-inch diameter reactor tube was used. During the growth process the reactor chamber is set at low pressure ($\sim 10^{-6}$ Torr) and heated up to 1000°C in hydrogen atmosphere. Methane is used as a carbon source (growth time is typically 10 min).

Graphene was transferred on titanium alloy surface and silicon nitride surface using “PMMA-mediated” method [26]. First, PMMA (495 K, about 100 nm thick) was spin-coated on top of the synthesized graphene on copper substrate and dried for 24 hours at room temperature. Next the graphene from bottom of Cu substrate was etched by reactive ion etching method in oxygen plasma (PlasmaLab 80+, Oxford Instruments). After that, the exposed Cu foil was dissolved in an aqueous etchant of iron (III) nitrate for several hours. When the copper is dissolved the graphene sample was cleaned in DI (deionized) water. Next, ion particles removing step was used with hydrochloric acid solution, hydrogen peroxide as catalyst dissolved in water [26]. After all cleaning steps PMMA/graphene layer was transferred on examined surfaces and annealed in order to evaporate the water and increase adhesion between graphene and the surface. In the last step PMMA layer was removed.

4. Test samples preparation

In the Figure 1 schematic procedures of the test samples preparation are shown.

B. Analysis of surface characteristics

The quality and number of transferred layers of graphene were evaluated by Raman spectroscopy (InVia Renishaw Spectrometer, 514 nm laser line, standard mode). All Raman spectra were collected at room temperature using 1 mW of laser power (on the sample).

Raman spectroscopy is a nondestructive and fast method for study e.g. various carbon materials. In case of graphene, Raman spectra gives information about number of layers [27], material quality and defects [28]. Typical Raman spectra consists of 3 main modes: D mode ($\sim 1350\text{ cm}^{-1}$), G mode ($\sim 1580\text{ cm}^{-1}$) and 2D mode ($\sim 2700\text{ cm}^{-1}$). Monolayer graphene sheet is easily identified by Raman study simply by looking at the G/2D relative intensity ratio (usually about 0.2), also taking into account the shape of those peaks [27]. The quality and defectiveness of graphene sheet can be verified by appearance of D mode peak, usually taken as the relative ID/IG ratio [29, 30].

The thickness of deposited hybrid systems was measured by Taylor Hobson Talysurf CCI Lite optical profilometer and was equal to 210 nm.

The elemental composition and the surface morphology of the silicon nitride coatings were investigated with the aid of Zeiss FE-SEM Merlin with EDS Quantax System (Bruker) scanning electron microscope.

C. Mechanical characterization

The hardness measurements of the obtained coatings were performed by the nanoindenter manufactured by CSM Instruments (Switzerland) equipped with a diamond Vickers indenter. The hardness was calculated using the method proposed by Oliver and Pharr [31]. Each data point represents an average of five indentations. A number of measurements were carried out for various depths of nanoindentation (from 80 nm to 700 nm). In order to measure the “film-only” properties and minimize the impact of the substrate, a method of nanoindentation measurements approximation was implemented [32].

D. Electrochemical measurements

Electrochemical measurements were carried out in 0.5 M/l NaCl, 2 g/l KF, pH=2 adjusted by concentrated hydrochloric acid. The solution (0.5 M NaCl, pH 2 2 g/l KF) in which the electrochemical measurements were conducted is characterized by a high corrosivity compared to titanium alloys. It is a more aggressive environment than that of typical electrolytes for corrosion tests (e.g. artificial saliva, SBF). Voltammetric measurements (polarization curves) were carried out at a scan rate of 1 mV/s within the range of -150 mV to 1000 mV versus open circuit potentials, and polarization curves corresponding to all examined material were recorded. Prior to each polarization experiment, the samples were immersed in the electrolyte for 1 h while monitoring open circuit potential to establish steady state conditions. Each electrochemical measurements for the same material, was performed for three times. In the paper we show only the most representative result. However, the differences between the successive values of the open circuit potential (for the same material) did not exceed 50 mV. A three-electrode cell arrangement was applied using the Ag/AgCl electrode with a Luggin capillary as reference electrode and a platinum wire as the auxiliary electrode (counter electrode).

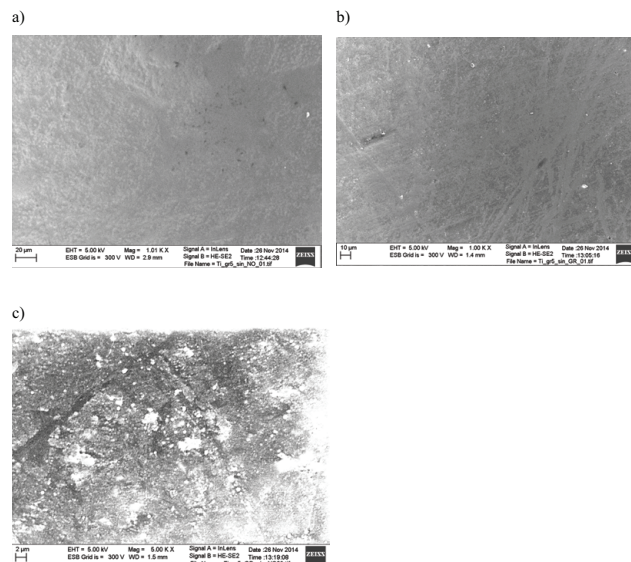


FIG. 2. SEM images of as-deposited coatings systems: a) SiN b) SiN/graphene and c) graphene/SiN

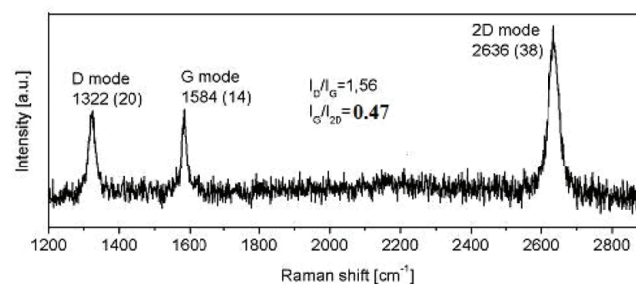


FIG. 3. Typical Raman spectra of Ti-Al-V/SiN/graphene system. The spectra was collected using the measurement parameters (633 nm laser line, 60 sec. of exposure time and two accumulations).

The measurements were carried out by means of an Autolab EcoChemie System of the AUTOLAB PGSTAT 302N type equipped with GPESv. 4.9. software in aerated solutions in room temperature. The values of corrosion current densities (i_{corr}) were obtained from the polarization curves by extrapolation of the cathodic and anodic branch of the polarisation curves to the corrosion potential [33].

III. RESULTS AND DISCUSSIONS

A. Structural characterization of Ti-Al-V/SiN, Ti-Al-V/SiN/graphene and Ti-Al-V/graphene/SiN coatings systems

SEM images of the surface of the coatings are shown in Figures 2 a-c. The SEM observation of the samples reveals interesting differences depending on the different composition of the following hybrid systems: SiN thin film (sample No. 1) and SiN/graphene (sample No. 2) were crack free, exhibited good adherence to the substrate, no discontinuous of the thin films was observed and the sur-

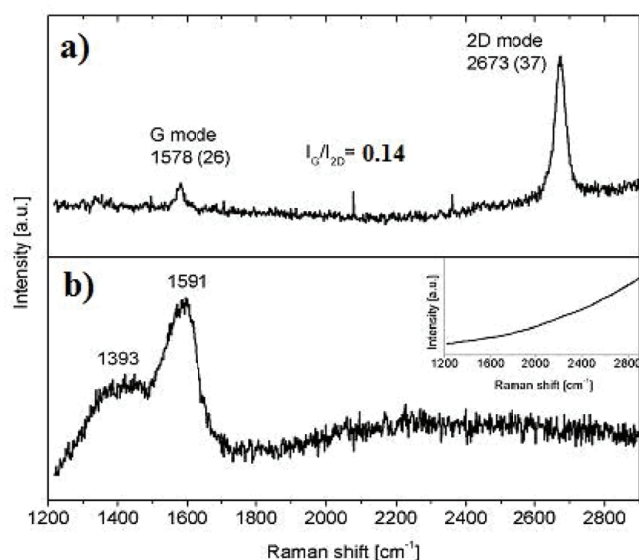


FIG. 4. Raman spectra of Ti-Al-V/graphene system (A) and Ti-Al-V/graphene/SiN system (B). The inset graph (B) shows typical Raman spectra of SiN coating graphene in range 1200–2900 cm^{-1} . All Raman spectra were collected using the same measurements parameters (514 nm laser line, 30 sec of exposure time and one accumulation).

face morphology was homogeneous (see Figs. 2a and 2b, respectively). Completely different results were obtained for the sample No. 3-TiAlV/graphene/SiN coatings system. The silicon nitride thin film deposited on the top of the graphene monolayer is peeled off. This suggests poor adhesion of the SiN thin film to the graphene monolayer surface (Fig. 2c).

B. Raman characterization of graphene layer in Ti-Al-V/SiN/graphene and Ti-Al-V/graphene/SiN coatings systems

Figure 3 shows the Raman spectra collected for the Ti-Al-V/SiN/graphene system. The G/2D ratios indicate that on the silicon nitride thin film surface exist a single layer of graphene [42, 43]. The quite big peak D ($\sim 1350 \text{ cm}^{-1}$) intensity indicates that obtained on surface single layer of graphene is defective.

For the Ti-Al-V/graphene/SiN system we first verified Raman spectra for graphene layer before deposition of SiN (Fig. 4a) where negligible D mode is seen suggesting that graphene layer is without structural defects. Moreover the intensity ratio of G and 2D modes shows that this is indeed a monolayer graphene.

After SiN deposition we found some areas where SiN layer peeled off from graphene surface forming some kind of holes in the SiN layer which suggests low silicon nitride adhesion to thin carbon layer. Raman spectra collected in those peeled off areas shows existence of amorphous carbon (Fig. 4b) [41, 42]. So, the SiN deposition process seems to strongly deteriorate the quality of deposited graphene, resulting in a shift of the electrochemical potential towards negative values (see Fig. 6b). The inset in Fig. 4b corresponds signal collected on SiN layer that

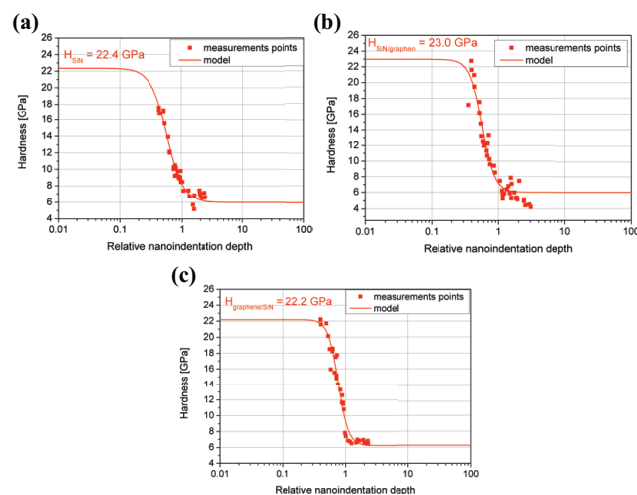


FIG. 5. Results of hardness investigation for a) SiN thin film, b) SiN/graphene coatings system and c) graphene/SiN coatings system.

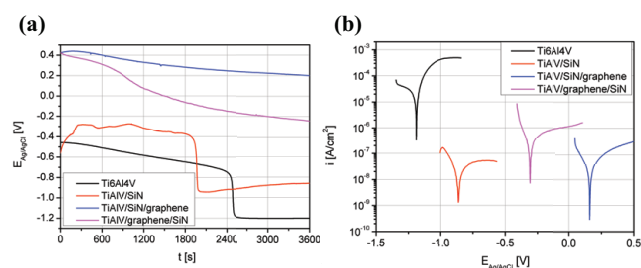


FIG. 6. Open circuit potential (OCP) (a) and polarization curves (b) of Ti6Al4V titanium alloy and titanium alloy with coating system.

supposed to cover graphene layer, but this time showing no evidence of carbon. This might be caused by the fact that SiN completely screens the Raman signal of carbon from the underlying layer, especially if this is an amorphous carbon layer which has usually lower intensity than graphene.

C. Mechanical characterization of prepared coatings systems

The hardness of prepared coatings systems was measured by nanoindentation and determined by an approximation method. For pure titanium alloy nanohardness have been measured at a constant depth equal 80 nm. It is the smallest depth, for which correct results have been obtained. Additionally, the root mean square error (RMSE) was calculated.

The hardness obtained for the uncoated titanium alloy (sample No. 4), silicon nitride thin film (sample No. 1), silicon nitride/graphene (sample No. 2) and graphene/silicon nitride (sample No. 3) coatings systems, was equal to $5.94 \text{ GPa} \pm 0.2 \text{ GPa}$, $22.4 \text{ GPa} \pm 0.5 \text{ GPa}$ (Fig. 5a), $23.0 \text{ GPa} \pm 0.5 \text{ GPa}$ (Fig. 5b) and $22.2 \text{ GPa} \pm 0.5 \text{ GPa}$ (Fig. 5c), respectively. As compared to the results presented in the literature reports, hardness of inves-

TABLE III. Corrosion tests results of Ti6Al4V alloy and Ti6Al4V alloy with coating system obtained from polarization curves in 0.5M NaCl, pH=2, 2g/l KF solution.

Sample	i_{corr} [A/cm ²]	E_{corr} [V]
TiAlV/SiN	5.8E-08	-0.866
TiAlV/SiN/graphene	5.1E-08	0.162
TiAlV/graphene/SiN	4.5E-07	-0.307
Ti6Al4V	6.1E-05	-1.188

tigated silicon nitride thin film is higher of ca. 51% [38–44] and 22% [45].

Graphene monolayer deposited on silicon nitride thin film (sample No. 2) and embedded between titanium alloy surface and silicon nitride thin film (sample No. 3) is practically not seen by nanoindenter during measurements. Therefore, the measurement did not reveal changes of silicon nitride thin films hardness on samples No. 2 and No. 3, in comparison with the silicon nitride thin film (see Figs. 5a-b and 5c).

D. Potentiodynamic tests

Figures 6a and 6b show the course of the open cell potential (OCP) and the course of polarization curves of titanium alloy and titanium alloys with coating system in 0.5 M/l NaCl, 2 g/l KF, pH= 2 electrolyte solution. The results of measurements of electrochemical parameters of the samples obtained from polarization curves are collected in Table III.

In the case of titanium alloy with coatings a significant improvement in the corrosion properties is seen, expressed by decrease of corrosion current density i_{corr} and shift E_{corr} values to the noble potentials. The smallest corrosion current density and the best corrosion properties, was obtained for the Ti6Al4V/SiN and TiAlV/SiN/graphene coatings systems. However, corrosion potential value for the TiAlV/SiN/graphene coatings system was $E_{\text{corr}} = 0.162$ V, which is much more positive than E_{corr} registered for the other samples. A positive value of the corrosion potential is characteristic for materials with low electrochemical activity and thereby very good corrosion resistance. It should also be noted that the course of potential is very stable. During one hour exposure the potential changed only by about 200 mV. For the sample covered by the SiN thin film despite the low value of i_{corr} a much more negative corrosion potential was observed. During exposure in the electrolyte solution, after about 1800 s a sharp decline in the value of the potential from -0.4 V to -0.9 V takes place. This is probably due to the penetration of the coating by the electrolyte and starts the corrosive reaction of titanium alloy. Similar course of OCP for titanium alloy without coating was observed. In this case after about 2400 s a sharp decline

in the value of the potential from -0.75 V to -1.20 V takes place. However, this change is caused by damage of the oxide layer present on the surface of a titanium alloy. The oxide layer acts a barrier and protection against general corrosion processes. However, in the environment of acidic pH (pH ca. 2) the protective layer is unstable and the processes of corrosion of metallic Ti or its alloys are initiated. This phenomenon is accelerated in the presence of aggressive ions such as fluoride ions. [34–37].

The value of corrosion current density obtained for TiAlV/graphene/SiN coatings system is higher than the values obtained for the TiAlV/SiN and TiAlV/SiN/graphene coatings systems. This is probably due by the poor quality of silicon nitride thin film.

The value of the corrosion potential, is located between values obtained for the TiAlV/SiN and TiAlV/SiN/graphene coatings systems. The more positive value of the corrosion potential than E_{corr} obtained for the TiAlV/SiN is due to the existence of the graphene layer at the structure interface, which blocking the access of the electrolyte to the titanium alloy. However, more negative value of this parameter than the value obtained for coating system with graphene monolayer on the top is probably due by the poorer quality of the graphene monolayer, than in the case of TiAlV/SiN/graphene coatings system. It should also be noted that the course of potential for the TiAlV/graphene/SiN coatings system is quite stable. During one hour exposure the potential changed only by about 600 mV.

IV. CONCLUSIONS

We have shown that SiN thin film, SiN/graphene and graphene/SiN coating systems deposited on titanium alloy surfaces, can be considered as a coatings that improve surface hardness of the Ti6Al4V alloy.

From the all three tested coating systems only the TiAlV/SiN/graphene and TiAlV/graphene/SiN systems can be considered as a barrier coatings systems for the Ti6Al4V alloy, protect it surface against corrosion processes, which take place on pure titanium alloy surface in very aggressive environments. Instead, only for the silicon nitride/graphene coatings system is not observed structural degradation during coatings system preparation.

In the next step, the durability of corrosion and mechanical properties of hybrid systems during temporary exposure in corrosive environments (artificial saliva, SBF etc.) investigations will be performed.

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