INFLUENCE OF SURFACE PREPARATION OF IMPLANTABLE Ti6AL4V ALLOY ON PROPERTIES OF Si-DLC AND DLC CARBON COATINGS

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Abstract

In the case of devices intended for permanent implantation, such as hip, knee and shoulder replacements or dental implants, a highly developed surface promotes the osteointegration process. In contrast, removable implants require a mirror-like surface to prevent tissue ingrowth and allow for non-invasive removal. The objective of this study was to analyze the influence of substrate pretreatment and the properties of DLC (diamond-like carbon) and Si-DLC (silicon-doped diamond-like carbon) coatings, including surface roughness, adhesion, chemical structure, and corrosion resistance. Surface preparation methods such as sandblasting and polishing, commonly used by implant manufacturers, and RFPACVD plasma modification of Ti6Al4V, a popular titanium alloy in the medical field, were used in the study. The results obtained show that regardless of the pretreatment method used to determine the characteristic roughness of the samples, they can be effectively modified with carbon coatings, both with and without silicon doping. Using Raman spectroscopy, it was shown that the pretreatments applied prior to the coating preparation processes did not affect the chemical structure of the coatings prepared within the same group. However, the chemical structures of the DLC and Si-DLC coatings differed. The application of silicon doping in the carbon coatings improved their adhesion to the surface, as did the application of a surface pretreatment by an etching process. Regardless of the surface preparation method, the carbon coatings primarily reduced the electroactivity of the surface, while the silicon doping present in them had a positive effect in shifting the corrosion potential to more positive values.

Keywords: *Ti6Al4V alloy, DLC, Si-DLC, surface preparation of medical devices*

Introduction

In Europe, one of the most popular alloys used in medicine is the titanium alloy Ti6Al4V, which is widely used mainly in orthopedics [1]. Medical devices made from this alloy have different surface finish requirements depending on the functions for which they are intended [2]. For example, when Ti6Al4V alloy is used in the manufacture of dental implants or endoprosthetic stems, its surface must be characterized by sufficient roughness [3]. Such a solution can facilitate the osteointegration process, allowing a permanent connection between the implant and the surrounding bone tissue [4]. Other surface requirements apply to orthopedic implants that temporarily support the bone healing process and stabilization [5]. The surface of bone plates or intramedullary nails should be smooth to minimize integration of the implant into the bone tissue. In addition, a polished structure reduces the risk of areas that favor the accumulation of infection-causing bacteria and prevents irritation of surrounding tissues [6]. The Ti6Al4V alloy is also used in the manufacture of medical instruments, where a sandblasting process is applied to the gripping parts, primarily to reduce the risk of slippage and increase comfort. The resulting surface development provides excellent light scattering when working in the surgical field without causing reflections [7].

Implants made of the Ti6Al4V alloy continue to enjoy uninterrupted success, mainly due to their high biocompatibility, paramagnetism, and exceptional strength-to-weight ratio [8]. Nevertheless, ions released from their surface during use, especially those of aluminum and vanadium, can adversely affect the patient's body [9]. However, this phenomenon can be reduced or eliminated by the use of coatings, such as diamond-like coatings [10]. On the other hand, as shown in the literature, the properties of DLC coatings are influenced by the method of surface pretreatment [11] and the type and content of additional elements introduced into their structure [12]. All these issues have been analyzed in the present work. The presented results show the influence of the pretreatment of Ti6Al4V alloy substrates by sandblasting, mechanical polishing and plasma etching on the properties of the deposited DLC and Si-DLC coatings. The study determined the surface roughness after the pretreatment processes and the deposition of carbon coatings, but also analyzed the changes in the chemical structure of the produced coatings using Raman spectroscopy. Their adhesion to substrates and the effect of the surface modifications used on the corrosion resistance properties obtained were evaluated.

Materials and Methods

Sample preparation

The study was carried out on Ti6Al4V alloy disks with a diameter of 16mm and a height of 7mm after three types of surface pretreatment: sandblasting, polishing and plasma etching. Sandblasting was performed at a pressure of 6-8 bar using an abrasive in the form of micro glass beads with a diameter of 70-110μm and a nozzle with a diameter of 8 mm. The polished substrates were ground on one side using SiC abrasive papers of the following grits: 80, 120, 320, 500, 600, 800, 1200, 2400 (Struers ApS), and then polished to a mirror-like finish using diamond paste with a grain size of 3μm (Struers ApS). Plasma etching was performed in a vacuum chamber using high-frequency plasma at a pressure of 8 Pa and an autopolarization potential of -1400 V.

Further modification involved the synthesis of two types of coatings: DLC and silicon-doped (Si-DLC). In both cases, the fabrication method was PACVD using a 13.56 MHz discharge (detailed process parameters are shown in TABLE 1). Prior to deposition, each sample was washed in acetone for 10 minutes using an Ultron U-506 ultrasonic cleaner to degrease the surface.

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TABLE 1. Process parameters for the synthesis of Si-DLC and DLC carbon coatings for the titanium alloy substrate material Ti6Al4V

Type of coatings	Durin etching				During fusion				Temprerture of modified surface
	Potential/ power	Pressure	Gas mixture (CH_4/HMDSO)	Time	Potential/ power	Pressure	Gas mixture (CH_4/HMDSO)	Time	
	[V]/[W]	[Pa]	[sccm]	[s]	[V]/[W]	[Pa]	[sccm]	[s]	[°C]
Si-DLC	-1400/900	8	0/0	900	-1000/1200	60	20/10	180	max. 550
DLC	-1400/900	8	0/0	900	-1000/1200	40	20/0	180	max. 520

Measurements of surface roughness and the thickness of the coating

The roughness and thickness of the carbon coating measurements were performed using a Hommel Tester T1000 contact profilometer (Jenoptik). Roughness evaluation was conducted on profiles of 10 mm in length, and the probe that was moving with a speed of 0.5 mm/s. Five measurements were taken for each sample, and the arithmetic mean was calculated. The thickness measurements involved the determination of the height of the step created by masking part of the sample with a silicon wafer during the coating deposition. The results, in the form of profilograms, were processed based on five measurements using the "Hommel Etamic EVOVIS mobile 2.00.1.00" software

Raman spectroscopy studies

The tests were carried out using a Renishaw inVia spectrometer with a 532 nm laser. This non-destructive method provides information on the chemical structure of the DLC and Si-DLC coatings produced. Each spectrum was deconvoluted in PEAKFIT 4.12 with Gaussian-Lorentzian functions together with a linear baseline correction corresponding to the D band (about 1350 cm^{-1}) and the G band (about 1580 cm^{-1}). Their position, the half-width of the G peak and the area ratio of the ID/IG characteristic bands were determined from the PEAKFIT data. The measurements were repeated five times in random locations on the surface of each sample.

Adhesion studies on DLC and Si-DLC coatings

Adhesion testing of silicon-doped DLC and Si-DLC coatings on polished and plasma-etched substrates was performed using a Nano Indenter G200 with the scratch test method. Sandblasted samples were not tested due to their high roughness. A diamond conical penetrator with an apex angle of 90° and a radius of curvature of 1 µm was used to measure adhesion. The scratch speed was 1 µm/s, the maximum loading force was 20 mN, and the scratch length was 100 µm (0.2 mN/µm). As a result of the experiments and scratch analysis using a Nikon Eclipse MA200 optical microscope, critical delamination force values were obtained for the tested coatings. The presented result were in fact the average of five measurements.

Corrosion testing

Corrosion tests were performed in a 0.9% NaCl solution in deionized water at 37°C. The solution was stirred and degassed with argon throughout the test. The electrochemical cell prepared for the corrosion experiments was of the three-electrode type (400 ml Corrosion Cell, Methrom Autolab) with a platinum electrode as the counter-electrode, a saturated calomel electrode (SCE, Elmetron, Zabrze, Poland) as the reference electrode, and the test sample (with an exposed surface area of 0.785 cm^2) as the working electrode. An Autolab PGSTAT 302N potentiostat controlled by NOVA 1.11 software (Metrohm Autolab B.V., Utrecht, The Netherlands) was used for electrochemical measurements. Prior to testing, samples were kept in solution for 3600 s to determine the free corrosion potential (Ecor). After stabilization of the corrosion potential, a potentiodynamic test was performed in the anodic potential range from 0.3 V below the Ecor potential to 1 V relative to the SCE at a scan rate of 1 mV/sec. The values of corrosion potential Ecor and corrosion current Icor were determined from the potentiodynamic curves.

Results and Discussions

Roughness

The results of the surface roughness measurements for the modified Ti6Al4V titanium alloys are expressed as the Ra parameter and are presented in TABLE 2. On this basis, it can be concluded that the sandblasting processes had the most significant influence on the surface development of the Ti6Al4V alloy, for which an Ra of 0.52 ± 0.03 µm was obtained. In comparison, mechanical polishing processes resulted in an Ra of approximately 0.04 ± 0.01 µm. The use of plasma etching increased the roughness of the polished samples to Ra 0.12 ± 0.01 µm. After the DLC and Si-DLC deposition processes, a decrease in Ra parameters is observed for the substrates with the highest roughness, especially after the sandblasting process. This effect can be attributed to the filling of larger irregularities by the coating. In most cases, and this is evident in the other samples, the DLC or Si-DLC coating accurately reflects the irregularities of the modified substrates without causing significant changes in the Ra parameter.

The thickness of the carbon coatings was similar for samples after mechanical polishing and plasma etching, regardless of whether the coating was doped with silicon or not. The average value was 110 ± 15 nm. Thickness measurements for samples after sandblasting were not possible. In this case, their roughness exceeded the coating thickness several times (see Ra parameter, TABLE 2), which did not allow for a precise baseline determination in the area of the step obtained via masking of the part of the sample during coating synthesis. Example profilograms for DLC and Si-DLC coatings are shown in FIG.1.

TABLE 2. Average Ra values obtained for the surfaces tested

Surface modification method	Ra [µm]
Mechanical polishing	0.04 (±0.01)
Mechanical polishing + DLC	0.06 (±0.02)
Mechanical polishing + Si-DLC	0.03 (±0.01)
Sandblasting	0.52 (±0.03)
Sandblasting + DLC	0.44 (±0.01)
Sandblasting + Si-DLC	0.49 (±0.02)
Plasma etching	0.12 (±0.01)
Plasma etching + DLC	0.11 (±0.01)
Plasma etching + Si-DLC	0.12 (±0.01)

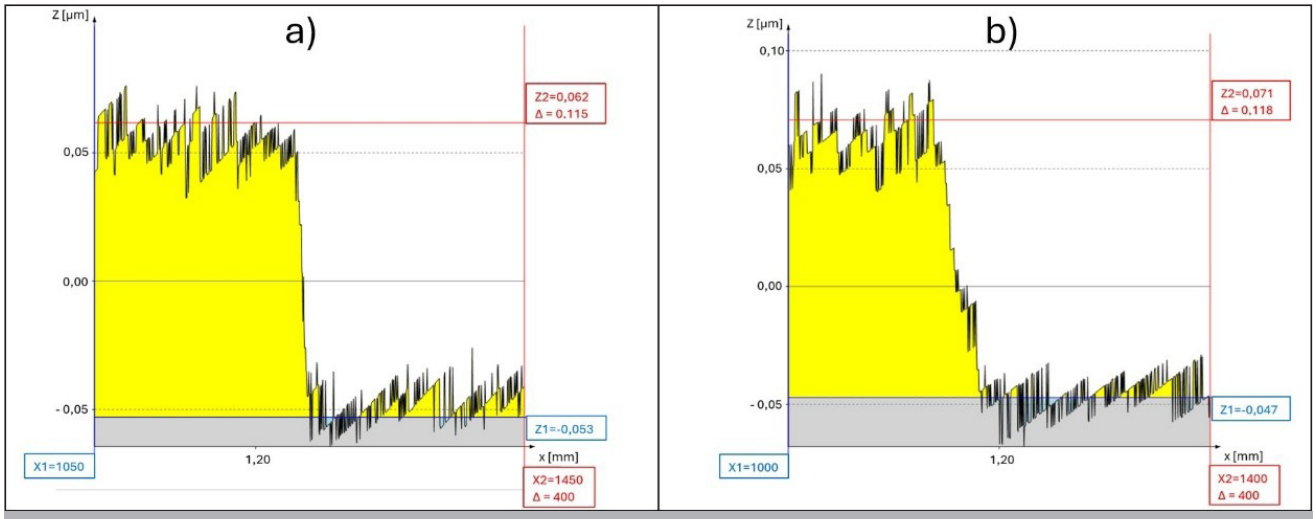


FIG. 1. Example profilograms allowing the determination of the thickness of carbon coatings for samples prepared by mechanical polishing and plasma etching for: a) DLC coating, b) Si-DLC coating.

Raman spectroscopy

The spectra obtained for various locations on each tested sample did not show any differences, which proves the high homogeneity of the chemical structure of the produced coatings. FIGs 2 and 3 show typical spectra characteristic of DLC and Si-DLC coatings produced for three different surface preparation methods. The results indicate that the pretreatment of titanium alloy substrates does not affect the chemical structure of the deposited carbon films. On the other hand, the comparison of the spectra of undoped and silicon-doped DLC coatings reveals changes in the intensity and half-width of the characteristic peaks, indicating possible differences in their chemical structure. This is confirmed by the data presented in TABLEs 3 and 4, especially the ID/IG ratio. For DLC coatings, the average value of the ID/IG ratio is 2.05, while for Si-DLC coatings it is 2.09.

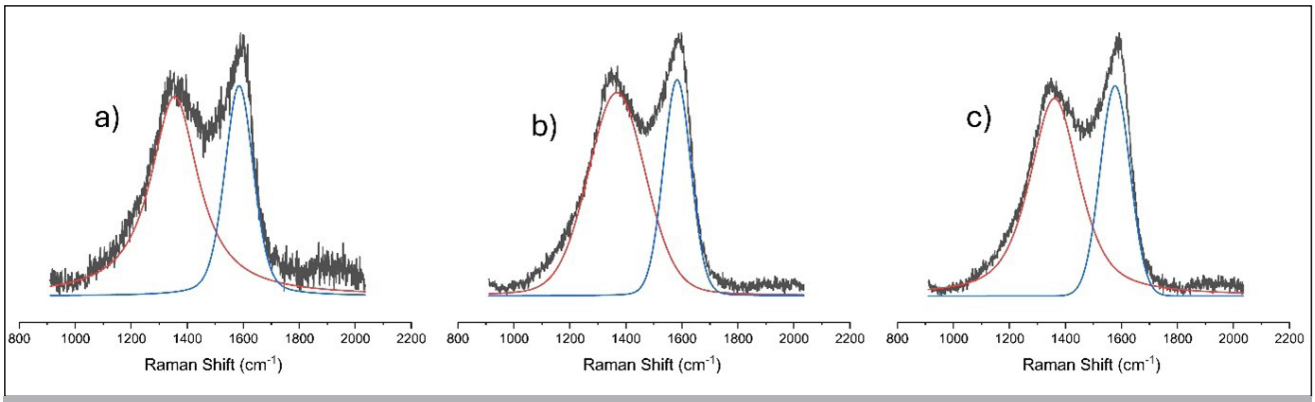


FIG. 2. Raman spectra from DLC coatings etched on Ti6AL4V titanium alloy substrate using different surface preparation methods: a) mechanical polishing, b) sandblasting, c) plasma etching

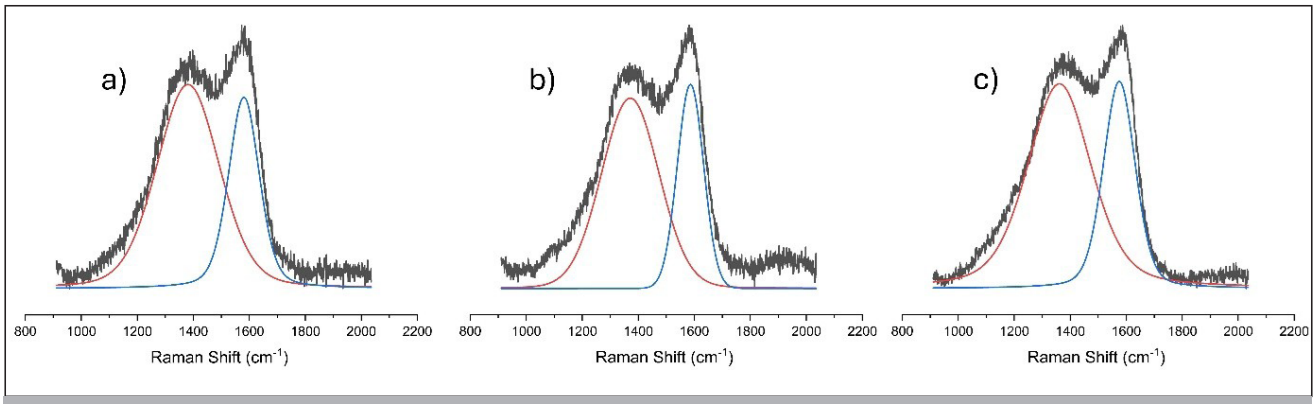


FIG. 2. Raman spectra of Si-DLC coatings rendered on Ti6AL4V titanium alloy substrate using different surface preparation methods: a) mechanical polishing, b) sandblasting, c) plasma etching

TABLE 3. Basic parameters of Raman spectra of DLC coatings rendered on Ti6AL4V titanium alloy substrate using different surface preparation methods: a) mechanical polishing (DLC 1), b) sandblasting (DLC 2), c) plasma etching (DLC 3)

Sample	ID/IG	G position (cm^{-1})	D position (cm^{-1})	FWHM of G peak (cm^{-1})
DLC 1	2.06	1585	1355	121
DLC 2	2.05	1583	1367	115
DLC 3	2.05	1577	1360	125

TABLE 4. Basic parameters of Raman spectra of Si-DLC coatings deposited on Ti6AL4V titanium alloy substrate using different surface preparation methods: a) mechanical polishing (Si-DLC 1), b) sandblasting (Si-DLC 2), c) plasma etching (Si-DLC 3)

Sample	ID/IG	G position (cm^{-1})	D position (cm^{-1})	FWHM of G peak (cm^{-1})
Si-DLC 1	2.09	1581	1381	129
Si-DLC 2	2.10	1586	1371	110
Si-DLC 3	2.09	1575	1361	134

Adhesion tests on carbon coatings

As a result of the scratch adhesion tests, the critical delamination force values for DLC and Si-DLC coatings were obtained and are shown in TABLE 5. These tests could not be performed on samples with sandblasted coatings due to the significant surface evolution.

From the values shown in TABLE 5, it can be concluded that the doping of the DLC films with silicon leads to an increase in their adhesion values compared to those of the DLC films without doping, regardless of the substrate preparation. It can also be concluded that the improvement of the adhesion of the carbon coating is influenced by the applied surface treatment of the Ti6Al4V alloys; higher adhesion values were obtained for samples that underwent mechanical polishing and plasma etching. These results are related, on the one hand, to the reduction of the intrinsic stress of the silicon-doped layers and, on the other hand, to the influence of the longer plasma exposure time on the substrate during the initial etching processes.

TABLE 5. Values of critical delamination forces

Subtrate treatment type	Coating type	Critical delamination force value [mN]	SD
Mechanical polishing	DLC	10.6	0.8
	Si-DLC	13.7	1.2
Mechanical polishing and plasma etching	DLC	13.9	1.2
	Si-DLC	15.5	1.3

Corrosion tests

The recorded potentiodynamic characteristics of the tested samples modified with carbon coatings showed some differences depending on the surface preparation method. Observing the curves in the region where the Tafel relation is fulfilled, it can be seen that the value of the corrosion current is in the range of a few to a few tens of nA for all measurements and does not show significant differences. Larger discrepancies are seen in the case of the corrosion potential, especially for samples prepared by polishing and sandblasting. In the case of polished samples (FIG. 4), we observe a favorable shift of the corrosion potential for the Si-DLC modified sample towards positive values of about 200 mV compared to the DLC coated and unmodified surfaces. The comparison of the sandblasted samples (FIG. 5) shows improved parameters for the carbon coatings. The corrosion potential value is about 200 mV higher than for uncoated samples, and the curves for DLC and Si-DLC modifications practically overlap. After plasma etching (FIG. 6), the values of corrosion currents and potentials reached similar levels, with a slight advantage for the Si-DLC coating.

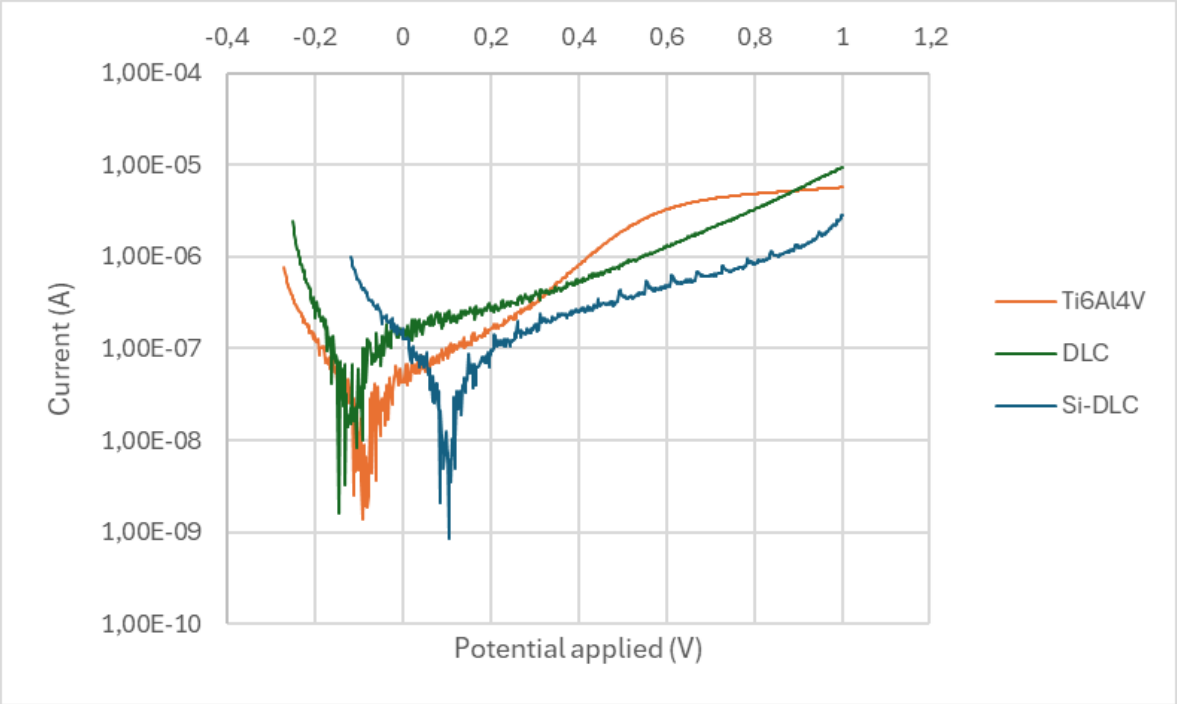


FIG.4. Anodic polarisation curves for titanium alloy unmodified and modified with carbon coatings, whose surface was prepared by mechanical polishing.

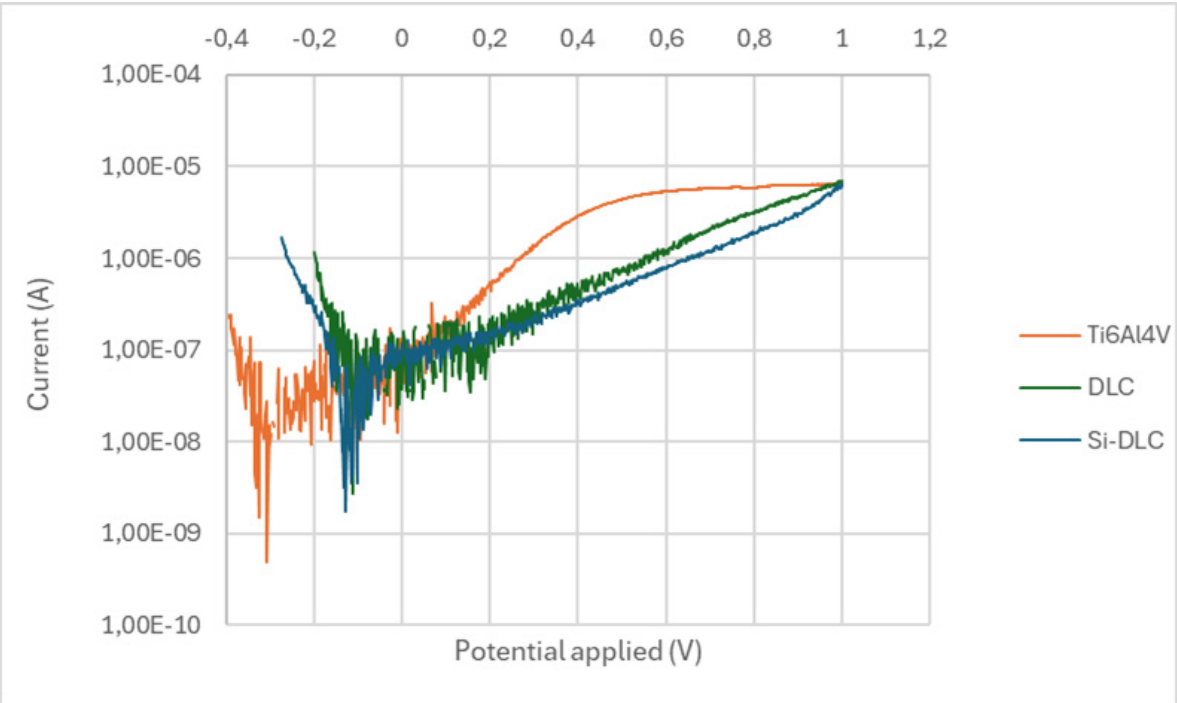
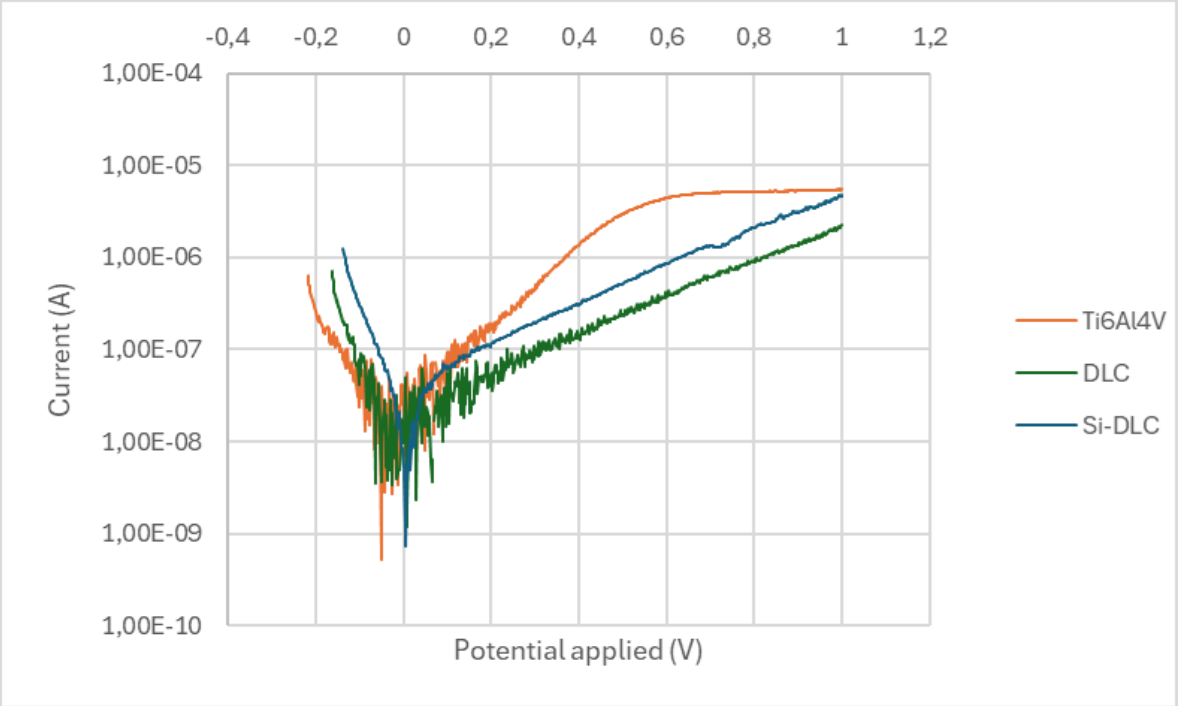


FIG.5. Anodic polarisation curves for titanium alloy unmodified and modified with carbon coatings, whose surface was prepared by sandblasting.



Anodic polarisation curves for titanium alloy unmodified and modified with carbon coatings, whose surface was prepared by plasma etching.

TABLE 5. Values of critical delamination forces

	Polished		Sandblasted		Etched	
	Ecor [mV]	Icor [nA]	Ecor [mV]	Icor [nA]	Ecor [mV]	Icor [nA]
Ti614V	-109	30	-331	4	-44	20
DLC	-128	59	-128	28	6	18
Si-DLC	85	28	-127	41	-54	5

Conclusions

This article presents the analysis of the effect of modifying Ti6Al4V alloy through sandblasting, polishing, and plasma etching on the properties of the deposited DLC and Si-DLC coatings. Selected methods of modification have practical applications in the production of medical devices, from implants to surgical instruments. The parameters analyzed include: surface roughness after pretreatment and carbon coatings, the chemical structure of the coatings using Raman spectroscopy, adhesion of the coatings to the substrates, and corrosion resistance of the samples before and after modification. The study demonstrated that, regardless of sample pretreatment and the significant difference in roughness, the proposed substrate material can be effectively modified with carbon coatings, both with and without the addition of silicon. It was also shown that different substrate pretreatment methods did not affect the chemical structure of the resulting layers; however, variations in the chemical structure were observed between DLC and Si-DLC layers.

Pretreatment was important in the improving of adhesion. DLC coatings deposited on the plasma-etched surface achieved a 20% enhancement of that parameter in comparison to those synthesized only on a surface prepared by mechanical polishing. This effect can be attributed to the more effective cleaning of the sample surface resulting from ion etching. The addition of silicon also resulted in a 20% improvement in adhesion compared to the bare DLC coating for the sample prepared by mechanical polishing and a 10% improvement for the ones after plasma-etching. Silicon had a positive effect on stress reduction, which was reflected in the obtained results of the coating adhesion to the substrates.

Examination of corrosion resistance has shown that carbon coatings, regardless of the tested surface preparation method, do not increase surface electroactivity. On the contrary, in most cases, they lead to a beneficial reduction in this parameter. This is particularly evident in samples subjected to sandblasting processes (commonly used in the medical industry), which are characterized by a less favorable surface condition in terms of corrosion

resistance. Comparing the two types of coatings, DLC and Si-DLC, it can be seen that silicon doping shifts the corrosion potential toward positive values. In summary, the research presented in this article clearly demonstrates that controlling the pretreatment of substrates before producing carbon coatings, whether doped with silicon or not, can influence the surface development, adhesion of the coatings to modified titanium alloy substrates, and their corrosion properties. The Raman spectroscopy results confirmed that the method described in that article guarantees the uniformity of the chemical structure of the manufactured DLC or Si-DLC coatings, regardless of the surface modifications used as a pretreatment.

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