Review paper

Si-DLC coating on the surface of the hip endoprosthesis

Powłoka Si-DLC na powierzchni endoprotezy stawu biodrowego

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Słowa kluczowe: endoproteza stawu biodrowego, Si-DLC, warstwa diamentopodobna domieszkowana krzemem.

Abstract

Current challenges regarding improving the materials used for implant production focus on improving mechanical strength, biocompatibility, bioactivity, and resistance to wear related to longer periods of prostheses use. The Polish company MEDGAL has patented a new type of bone implant coatings covered with a Si-DLC (silicon-carbon) layer. It is characterised by a carbon layer with a silicon fraction of +3/+5%. The process of chemical vapour deposition assisted by high-frequency plasma RF PACVD was used for production. The advantages of the method used are low process temperatures that do not cause structural changes, and thus there is no risk of intergranular corrosion. Carbon and carbon-silicon layers of high purity and homogeneity were obtained. Thanks to the use of a silicon particle, the proliferation of osteoblasts is stimulated. Silicon is also responsible for the increase in the expression of genes that stimulate the formation of ossification thanks to GMP-2 and may affect the stimulation of type I collagen synthesis.

Streszczenie

Aktualne wyzwania dotyczące udoskonalenia zastosowanych materiałów do produkcji implantów koncentrują się na poprawie wytrzymałości mechanicznej, biokompatybilności, bioaktywności oraz odporności na zużycie związanej z dłuższymi okresami użytkowania protez. Polska firma MEDGAL opatentowała nowy rodzaj powłok implantów kostnych pokrytych warstwą SI-DLC (krzemowo-węglową). Charakteryzuje się ona warstwą węglową z frakcją krzemu +3/+5%; do produkcji wykorzystano proces chemicznego osadzania z fazą gazową wspomagany plazmą wysokiej częstotliwości RF PACVD. Zaletami zastosowanej metody są niskie temperatury procesu, które nie wywołują zmian strukturalnych, a tym samym nie występuje ryzyko wystąpienia korozji międzykrystalicznej. Uzyskano warstwę węglową i węglowo-krzemową o wysokiej czystości i jednorodności. Dzięki zastosowaniu cząsteczki krzemu dochodzi do stymulacji proliferacji osteoblastów. Krzem odpowiada także za wzrost ekspresji genów stymulujących tworzenie kostnienia dzięki GMP-2 oraz może wpływać na stymulacje syntezy kolagenu typu I.

Introduction

Hip arthroplasty is one of the greatest achievements of orthopaedic surgery. The primary goal of treatment is to reduce pain and improve the patient's locomotor function. The surgical methods and materials used for the production of implants enable a faster recovery of physical fitness and undertaking of professional work [1, 2]. An appropriately selected physiotherapy programme is also important. This usually involves rebuilding muscle strength and coordination, learning locomotion, and improving central stabilisation [3].

The biomaterials used to cover medical implants should meet the highest requirements. First of all, they may not cause inflammatory reactions in the surrounding tissues. Biotolerance and adhesion, as important mechanical characteristics, determine the suitability of carbon as a material for covering medical implants. The use of carbon became possible thanks to the development of a low-pressure method for the synthesis of diamond and diamond-like carbon layers [4].

Figure 1. Macroscopic photo of the Ti6Al4V alloy prosthesis after the APS modification process with porous titanium

Current challenges regarding the improvement of the materials used for the production of implants focus on improving the mechanical strength, biocompatibility, bioactivity, and wear resistance associated with longer periods of use of the prostheses [5].

Periprosthetic osteolysis is one of the main complications after implantation of a hip endoprosthesis. It is the result of an innate immune response caused by the wear of the supporting surfaces of the endoprosthesis. Tribocorrosion, i.e. the simultaneous wear of the material with corrosion, facilitates the formation of inflammation, which activates osteoclasts and contributes to the loosening of the endoprosthesis. Mechanical loosening of the endoprosthesis was the main cause of hip revision surgeries in 2008–2013 [6, 7].

Titanium and its alloys, as a material with mechanical properties similar to bone, are the basic building blocks of orthopaedic implants. At the same time, it shows poor tribological properties, including a high coefficient of friction and adhesive contact between the surfaces. Studies aimed at improving the mechanical and physicochemical properties of the prostheses focus mainly on modifications of the surface of the Ti6Al4V titanium alloy, which is the main material used for the mandrels of the prostheses. Surface modifications focus mainly on the production of coatings that improve adhesion to tissue (porous titanium), improve biocompatibility, bactericidal, or bacteriostatic properties (hydroxyapatite, carbon and oxide coating often with addition of, e.g., silver, copper, etc.) [8, 9].

This paper presents the first application of a hip prosthesis modified simultaneously with porous titanium and a carbon layer doped with silicon. So far, porous mandrel covers have mainly been associated with hydroxyapatite. The previous experience of the authors with the use of the Si-DLC layer in medicine is related to its application on smooth orthopaedic implants made of austenitic steel or titanium alloy. The layer was produced on electropolished surfaces, and its residence time in the body did not exceed 2 years. The experience gained allowed for the development of a technology for producing a composite coating on the surface of pins made of Ti6Al4V alloy, consisting of porous titanium produced by the APS method and a carbon layer doped with silicon by the RFPACVD method. The tests of physicochemical and biological properties enabled obtaining a certificate allowing the use of these prostheses [10]. Such an innovative coating combines the synergy effect resulting from the porous titanium improving the osseointegration, bacteriostatic, anti-allergic effect and increasing the biocompatibility of the Si-DLC layer [7, 11–14].

The aim of the study was material characterisation of the batch of prostheses produced for implantation and preliminary clinical observation after the implantation process. The further goal is long-term clinical observation, which will allow for a full characterisation of the healing process and durability of the prostheses.

Methods

A Medgal prosthesis made of Ti6Al4V titanium alloy and modified with a layer of porous titanium and carbon with addition of silicon was subjected to the tests. A layer of porous titanium was applied to the sandblasted surface of the prosthesis using the APS (atmospheric plasma spraying) method. The production of the porous titanium coating consisted of 2 passes of the plasmatron, with powders of 90–250 µm in size in the first pass and 25–90 µm in the second pass. In both cases, the velocity of the plasma stream was in the range of 350–450 m/s, and the amount of powder fed was 50–100 g/min. A macroscopic photo of the prosthesis after the modification process with porous titanium is shown in Figure 1.

After producing porous titanium on the surface, the prosthesis was subjected to the second stage of modification: the formation of a silicon-modified diamond-like coating (Si-DLC). The coating was produced by means of the PACVD method (plasma assisted chemical vapour deposition), in accordance with the patent of the Polish Patent Office No. 223008 of 3 November 2015 entitled "Method of producing a silicon-containing carbon layer on medical implants". The process was started with surface activation by etching in plasma with a frequency of 13.56 MHz and a pressure of 8 Pa, then a carbon-silicon layer was deposited in the methane band and vapours of organosilicon compounds, which are the source of carbon and silicon ions, respectively. The precursors were supplied at the same time and in the amount selected so that the pressure in the reactor chamber was from 30 to 60 Pa. Process parameters are given in Table 1.

Macroscopic photos of the prosthesis with a composite coating consisting of porous titanium and a Si-DLC layer and during the PARF CVD process in high-frequency plasma are shown in Figures 2 and 3.

The produced coatings were subjected to basic characterisation of their surface using optical microscopy, SEM Raman spectroscopy, computed microtomography, and a contact profilometer.

Microscopic tests were carried out on a VHX-KEYENCE VHX 950F optical microscope to determine the degree of accuracy of covering the surface of the samples with modified coatings. Observations were made in the magnification range from 100× to 700×

Table 1. Parameters of the Si-DLC layer synthesis process for the Ti6Al4V titanium alloy substrate material

Negative electrode polarization potential		Parameters of the plasma environment		Modified surface temperature [°C]
Etching [V]	Layer synthesis [V]	Pressure [Pa]	Composition of the gas mixture (CH4/HMDSO) [sccm]	
Max. 1400	900–1000	8–60	10–20/5–15	450–550

using a beam of light falling at different angles, which allowed for a more accurate analysis of the surface in terms of possible discontinuities. Tests of the surface topography of the samples were made using the JEOL JSM-6610LV scanning microscope. SEM analysis was performed from the surface of flat samples at magnifications of 100, 400, and 1000×. The surface roughness of the samples was measured using a Hommel Tester T1000 contact profilometer. The tests were carried out on a measuring section of 8 mm. For each of the samples, tests were performed 5 times to plot the average values of Ra, Rz, and Rmax. To determine the porosity, the non-destructive method of computed microtomography (CT) was used. The tests were performed on a SkyScan 1272 device (Bruker, Belgium) applying the following scanning conditions: X-ray source voltage 90 kV; X-ray source current 111 µA; and pixel size 6.7 µm. The rotation step of 0.2° was used, and an Al (0.5 mm) + Cu (0.038 mm) filters were selected. Optical microscopy studies were performed on the prosthesis, while the remaining tests were performed on flat samples produced in the same processes as the prosthesis.

The chemical structure of the DLC coatings was investigated using an inVia Confocal Raman Microscope (Renishaw, Gloucestershire, UK). All measurements were made using a 532 nm laser and 50× objective. Investigations were carried out in the spectral range from approximately 900 to 2000 /cm. Further analysis of the spectra was performed in PeakFit software (Version 4.12, Seasolve, San Jose, CA, USA) to deconvolve the spectra into 2 characteristic peaks D and G.

Results and discussion

Characteristics of modified surfaces

Microscopic analysis of the surface of the prosthesis after the first stage of modification, i.e. with porous titanium, shows a clear boundary between the substrate (protected against modification) and the coating produced, while the remaining modified surface shows no uncovered areas, which proves that the process was properly carried out. In the case of a prosthesis modified with a Ti coating and then Si-DLC, it was found that the carbon layer tightly covered the entire surface, reproducing the previously applied Ti coating (Figure 4).

The SEM analysis of the surface of the modified Ti6Al4V + Ti and Ti6Al4V + Ti + Si-DLC samples shows a similar topography, and their surface is irregular and shows signs of strong development (Figure 5).

Figure 2. Macro photo of the Ti6Al4V alloy prosthesis after the modification process with porous titanium using the APS method and the Si-DLC coating using the RF-PACVD method

Figure 3. The prosthesis during surface modification with the Si-DLC layer using the PA RF CVD method

The results of the roughness measurement confirm the microscopic and SEM observations that the Si-DLC layer produced on the substrate previously modified with porous titanium (Ti6Al4V + Ti), due to its thickness, has a slight effect on the roughness profile (Table 2).

The tests carried out using the computer micro tomography technique showed that after the process of producing the Si-DLC coating, there was a slight increase in the thickness of the porous layer (Table 3). However, it should be noted that these are only estimates for specific samples, and their value depends on the process parameters and thickness of the Ti layer (dispersion according to the manufacturer 50–250 µm). Samples with Ti6Al4V + Ti and Ti6Al4V + Ti + Si-DLC showed similar porosity of approx. 44%, which proves that with high roughness and porosity of the porous titanium layer, the Si-DLC layer influence on this property (Table 3).

The analysis of the chemical composition with Raman spectroscopy (Figure 6) after deconvolution

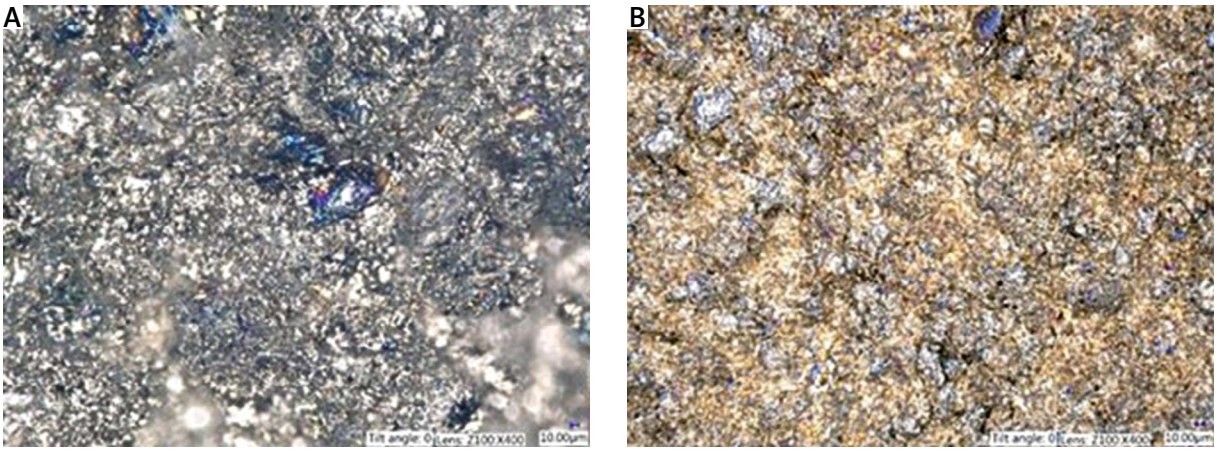

Figure 4. Microscopic photos of the surface of the samples: Ti6Al4V + porous Ti (**A**) and Ti6Al4V + porous Ti +_Si-DLC (**B**)

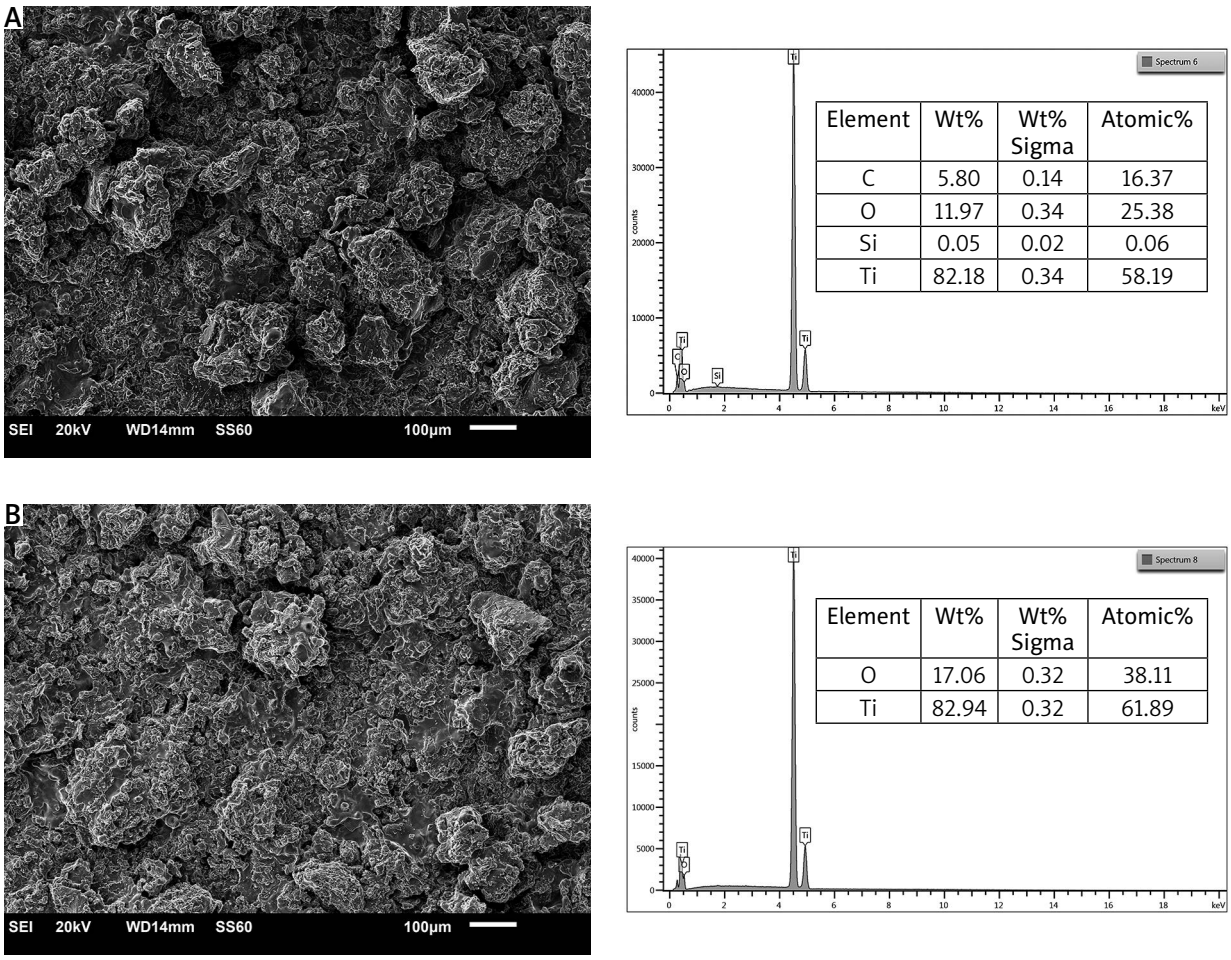

Figure 5. SEM image of the surface of the samples: Ti6Al4V + porous Ti (**A**) and Ti6Al4V + porous Ti + Si-DLC (**B**)

showed the existence of 2 characteristic peaks: D at the position of about 1360 ±10/cm and G at the position of about 1583 ±10/cm. Based on them, the ID/IG ratio of 2.03 ±0.02 was determined. In the case of Si-DLC coatings, the compatibility of the obtained spectra produced on finished medical devices with the layers on specially prepared samples was observed. The results showed a high repeatability of the coatings produced, regardless of the place on the mandrel and the chemical structure characteristic of diamond-like coatings.

Table 2. The results of roughness measurement using the contact method

Measurement	Measurement mean		Standard deviation	
	Ti6Al4V + Ti	Ti6Al4V + Ti + Si-DLC	Ti6Al4V + Ti	Ti6Al4V + Ti + Si-DLC
Ra [µm]	18.84	19.30	1.69	1.17
Rz [µm]	90.27	95.01	7.07	6.42
Rmax [µm]	124.13	138.12	9.41	13.03

Table 3. Results of the analysis of selected parameters of the internal structure of the samples

Layer	Ti6Al4V + Ti	Ti6Al4V + Ti + Si-DLC
Results of roughness measurement using the contact method [µm] (manufacturer's data)	50÷250 (Ti)	50÷250 (Ti)
Thickness of the porous layer, d [µm]	227	254
Porosity of the modified surface [%]	43.84	44.25
Open pores [%]	43.72	44.16
Closed pores [%]	0.09	0.12

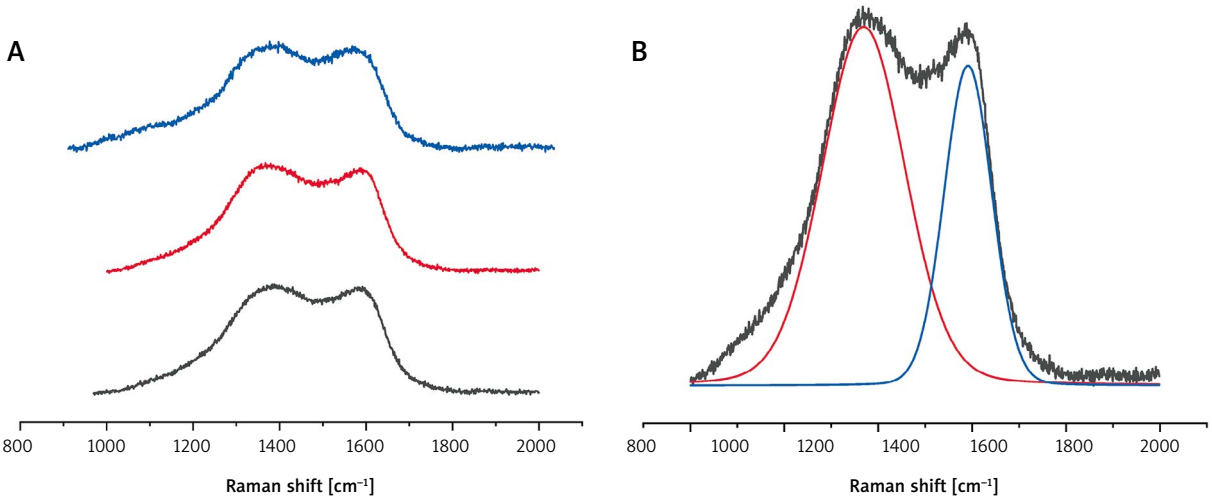

Figure 6. Examples of Raman spectra: for three different places of the Si-DLC coating produced on the Ti6Al4V_Ti_SiDLC composite prosthesis (**A**) and after deconvolution into two files (**B**)

A case study of use of a modified prosthesis

The conducted tests of physicochemical and biological properties allowed the company to obtain EC certificate No. 1434-MDD-091/2020 and to use prostheses with a composite layer of porous titanium and a diamond-like layer doped with silicon in medical practice. Currently, several dozen modified prostheses have been implanted, including the case of an 82-year-old patient after a paratrochanteric fracture of the right femoral neck, treated surgically. The original treatment consisted of stabilising the fracture with a Gamma nail on 21 July 2021. After a period of 14 months, the femoral neck screw migrated outside the femoral head, drilling into the hip socket (Figure 7).

The most common reasons for migration of the fixation described in the literature include unstable type of fracture, non-anatomical reduction of the fracture, or incorrect position of the intramedullary nails [13]. In addition, fractures of the femoral neck pose a risk of avascular necrosis (AVN) of the femoral head [15]. In the case of the described patient, there were no signs of necrosis of the femoral head in the X-ray imaging.

In the revision surgery, after the removal of the supplementary material, an endoprosthesis covered with the Si-DLC carbon-silicon coating by Medgal was implanted (Figure 8).

On the third day after the surgery, the patient was discharged from the ward in good general condition. Currently, the patient is under the supervision of an orthopaedic clinic. The recovery process is normal, and the ability to perform activities of daily living (ADL) has returned to its pre-injury state.

Figure 7. Migration intramedullary fixation (own source)

Figure 8. X-ray with endoprosthesis with carbon-silicon coating of the hip joint (own source)

Conclusions

The tests of hip joint endoprostheses modified with composite coatings of porous titanium and a diamond-like layer doped with silicon (Si-DLC) showed good physicochemical properties (porosity, roughness, chemical composition, etc.). Titanium and carbon coatings showed high uniformity of properties over the entire modified surface and good mechanical properties, which, together with the biological tests carried out in the certification process, allowed them to be used in practice. The developed and applied technologies for the production of coatings have shown that, regardless of the size and shape of the prostheses (from a given series of types), the quality and condition of the surface after the application of the Si-DLC layer is always the same. The use of carbon-silicon coatings on the surface of hip endoprostheses is an innovative material engineering solution in line with the direction of research carried out in many centres. Clinical experience to date includes several dozen cases of endoprosthesis implantation, with the longest observation period of 1 year. The results are very promising and require further observations regarding the wear processes of the applied coatings.

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Ethical approval

Not applicable.

Conflict of interest

The authors declare no conflict of interest.

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