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INVESTIGATION OF GLASSY CARBON COATING DEPOSITED ON TITANIUM ALLOY: MICROSTRUCTURE AND MECHANICAL PROPERTIES

VLADIMIR PETKOV[1], MIHAELA ALEKSANDROVA[1],
VESELIN PETKOV[1], DIMITAR TEODOSIEV[2],
ANNA BOUZEKOVA-PENKOVA[2*]

[1]*Bulgarian Academy of Sciences, Institute of Metal Science, Equipment and Technology with Hydroaerodynamic Center, "Acad. Angel Balevski", 67 "Shipchenski Prohod" Blvd, 1574 Sofia, Bulgaria*
[2]*Bulgarian Academy of Sciences, Space Research and Technology Institute, 1. "Acad. Georgy Bonchev", 1113 Sofia, Bulgaria*

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ABSTRACT: The deposition of glassy carbon coating on the widely applied in implantology titanium alloy – Ti 6V 4Al, is performed by a novel original thermo-chemical method, developed in the Bulgarian Academy of Sciences. The deposition of glassy carbon was carried out in a protective inert environment of argon at high temperature around 1000°C. The combination of biocompatible carbon containing coating and biocompatible titanium alloy represents an innovative implant material for medical use. An important aspect of the new material development process is the study of the mechanical properties and microstructure. Therefore, the microstructure and the mechanical characteristics of the obtained composite biocompatible material, consisting of titanium matrix and glassy carbon coating, were studied in the present work. The microstructure of the coating and its elemental composition were examined by metallographic microscope and by SEM-EDS analysis. Mechanical tests have also been performed in order to determine and compare the ultimate tensile strength and tensile yield strength of titanium alloy samples with and without glassy carbon cover. The hardness and the modulus of elasticity of the considered materials are determined by instrumented indentation technique.

KEY WORDS: biocomposite, titanium alloys, glassy carbon coating/layer/, microstructure, tensile strength.

*Corresponding author e-mail: a_bouzekova@space.bas.bg

1 Introduction

The vast majority of implants used in medicine are made of metallic materials. Metal implants are extremely important in repairing or reconstructing of damaged hard tissues in the human body. The main requirements for the characteristics of the implant materials are the following: low elastic modulus, high strength, excellent corrosion resistance and wear resistance, very good biocompatibility.

Among the metallic materials, titanium and its alloys are considered to be the most suitable materials for biomedical applications, due to their superior properties, which correspond completely to the requirements for implants. According to the world standards; titanium and its alloys possess better characteristics for implant application than other alternative materials, such as stainless steels, Cr-Co alloys, industrially pure niobium and tantalum. The main objective of this investigation is development of new technology for synthesis of new bio-composite, appropriate for implants, consisting of bio-titanium alloy covered with biocompatible glassy carbon. The deposition of glassy carbon (CB) on the titanium substrate carried out by a novel original thermo-chemical method, developed in our laboratories in the Bulgarian Academy of Sciences. The titanium alloy has been pretreated by depositing of plasma porous titanium, as described in [1]. Meanwhile, porous titanium-based alloys are being intensively developed as an alternative material for orthopedic implants, as they can provide good biological fixation by growing the bone tissue into the porous network [2].

It is well-known that the human body is appearing to be a complex biochemical and electrochemical system, containing corrosive acidic and basic liquids, aggressive towards implants. Body fluids contain different types of corrosive substances, like HCl, NaCl, KCl,O_2, CO_2, etc.; and the body implants are exposed to their continuous effect for years, therefore, the corrosion resistance is one of the main characteristics that implant materials have to possess. Poor corrosion resistance towards body fluids may lead to release of bio-incompatible metal ions from the implant, which is a major factor causing allergic and toxic effects [3].

The corrosion processes taking place in implant materials leads to overall implant disintegration, which in turn cause harmful effects on the surrounding tissues and organs. The presence of surface irregularities increases the implant functional area as well as the total degree/extent of corrosion. Surface treatment is an important method to improve implant corrosion resistance, and therefore, it leads to enhanced implant biocompatibility [4]. In addition, wear resistance mainly determines the operation lifetime of the implant, whereas the low wear resistance leads to implant loose, separation of fine metal particles and further inflammation of the adjacent tissue [5]. Ti-based alloys with a high friction coefficient could lead to formation of wear debris, thus causing inflammatory reactions and hence to loosening of the implant [6]. In summary, the development of implants with high corrosion and wear resistance is of great importance for enhanced longevity/lifetime of biomaterials in the human body. Internal tissue is formed between the bone and the implant, if the implant is not well integrated with the bone [7].

Therefore, implant material surface characteristics are essential for the successful implant integration with the adjacent bone. Surface chemistry, surface roughness and surface morphology play important role for complete osseointegration. In order to avoid long term problems with implants, we decided to cover selected titanium alloy with a high-class biocompatible material such as glassy carbon, also known as three-dimensional graphene [8]. In other words, the production of a bio-composite from two biocompatible materials is planned. Notably, biomaterial is a material that the human body is able to sustain for a long time without having harmful effects. This innovative material could be used for the manufacture of various implants, e.g. construction of prostheses, and for other purposes.

Vitreous carbon, also known as glassy carbon, can be produced in various forms. These products can be used for chemical analysis and preparation of fluorophosphate and other glass-like materials. The crucibles made of glassy carbon material are also used for growth of single crystals and other materials of extremely high purity. Glassy carbon shows excellent biocompatibility with living tissues, which means that it has great potential for applications in life and medical research in general [9].

2 Experimental

The titanium samples used in our study are in the form of punch with dimensions 20 mm in diameter and 10 mm in height, as well as in the form of profiled rifled/screwed/threaded rods/cylinders with diameter of 10 mm (Fig. 1). Glassy carbon is applied on the titanium samples by a thermo-chemical deposition and subsequent pyrolysis in protective inert argon gas environment. This process is carried out at a

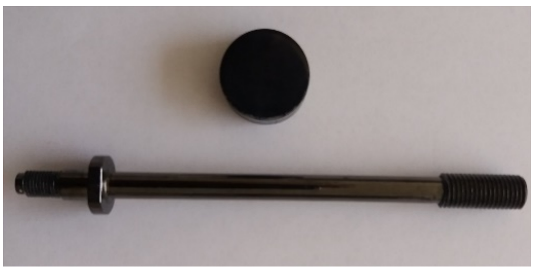

Fig. 1: Samples of titanium alloy Ti6Al4V covered with glassy carbon (GC).

temperature of about 1000°C. The thermo-chemical pyrolysis procedure can be repeated many times until a certain thickness of the glassy carbon layer is attained. Typically, in one run of this procedure, a layer about 1 μm thick is deposited.

2.1 MICROSTRUCTURE AND COMPOSITION

The micrographs were taken using a Cnoptec MIT 500 microscope connected to a DV 500 digital camera and a computer, whereas a magnification up to $\times 1000$ is used.

The microstructure of the cylinder and punch-shape titanium samples covered with glassy carbon (GC) were photographed. Figure 2 shows the microstructure of the cylinder-shape sample with a diameter of 5 mm and a thickness of the internal glassy carbon coating about 1.2 μm external. The magnification is $\times 100$.

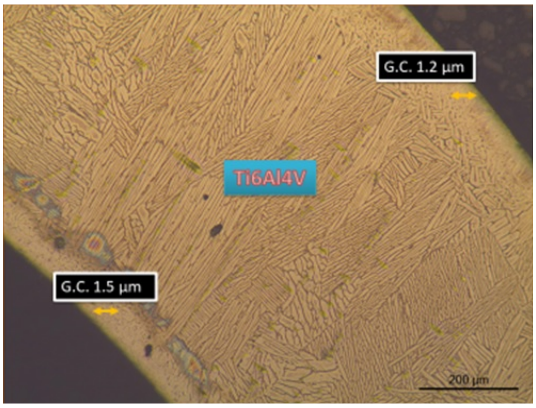

Fig. 2: Microstructure of a rod-shape sample of titanium covered with glassy carbon.

The Vickers micro-hardness has been determined with a MicroDuromat 4000 device from Reichert-Jung. The load is 0.03 MPa, load time is 10 s and the constant load retention time is 10 s. The results obtained are shown in Fig. 3. It shows the microstructure of a titanium alloy sample (substrate) covered with a thin layer of glassy carbon of about 1 μm. The determined micro-hardness of the substrate is about 5380 MPa. Due to the small thickness of the glassy carbon layer, its micro-hardness cannot be determined directly. Figure 3 clearly shows that the imprint of the diamond pyramid, located in the area of the glassy carbon layer and giving a micro-hardness of 2471 MPa, affects the substrate, the layer and the resin covering the surface of the sample. Obviously, this results for the hardness of the glassy carbon layer cannot be reliable and the hardness of the glassy carbon coating must be determined by another method.

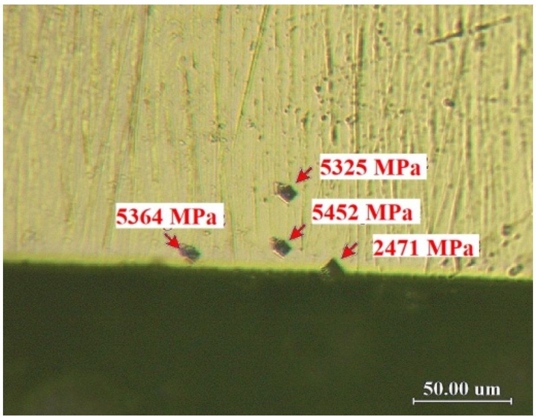

Fig. 3: Microstructure and micro-hardness (Vickers) of a titanium sample covered with glassy carbon.

Further studies on the microstructure of titanium samples covered with glassy carbon were performed using a scanning electron microscope "HIROX SH-5500P" with EDS system "QUANTAX 100 Advanced" Bruker.

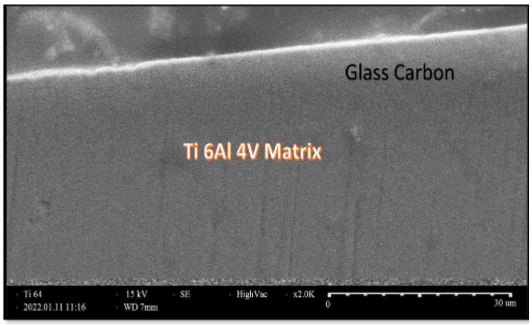

Fig. 4: SEM image titanium covered with glassy carbon.

The thin white stripe in Fig. 4 and Fig. 5 is the glassy carbon coating deposited on the titanium substrate and captured at a magnification of $\times 2000$. The coating layer is continuous, dense and uniform with a thickness of about 1.5 μm.

The SEM-EDS analysis established the content of the elements in the substrate (bulk material) and in the coating. Figure 6 shows the change of element content while passing from the bulk material to the glassy carbon layer. Figure 7 depicts the spectra of the chemical elements in colors. The elements are given in colors as follows: titanium (Ti) is in yellow, vanadium (V) is in orange, aluminum (Al) is in violet, carbon (C) is in blue color. We are interested in the part between 8.5 μm

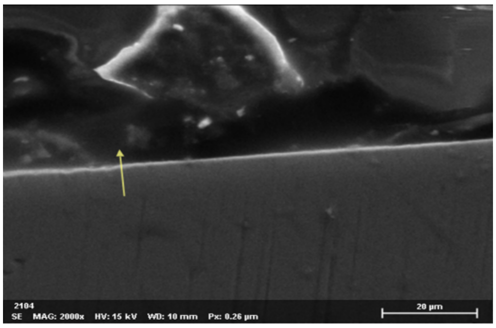

Fig. 5: SEM image of the titanium substrate covered with glassy carbon.

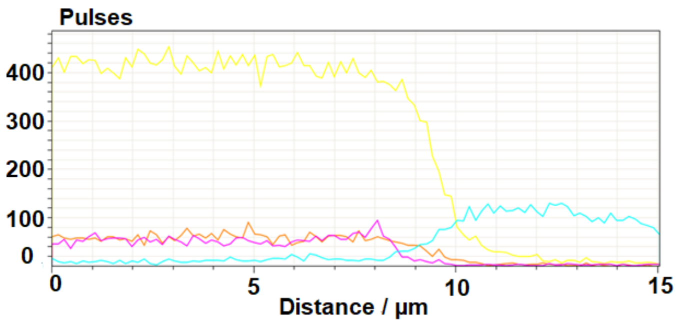

Fig. 6: Chemical content.

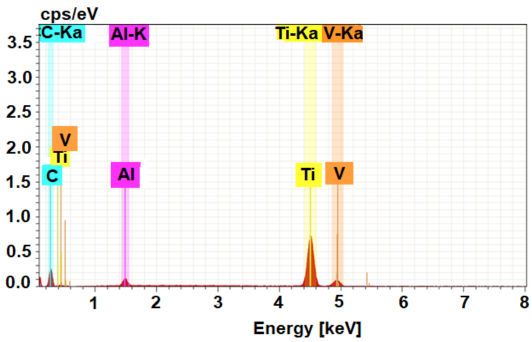

Fig. 7: Spectra of the elements in the substrate and the glassy carbon coating.

and 10 μm of the section, where there is a visible increase in the carbon curve and a decrease in the other curves. This proves that in this part there is located the glassy carbon layer and its thickness is of about 1-1.5 μm.

2.2 Mechanical testing

Figure 8 shows samples of titanium cylinder-shape samples covered with glassy carbon after tensile testing.

Fig. 8: Titanium rods after tensile testing.

Tests on titanium alloy samples in order to determine their physical and mechanical properties, according to the standard for spinal implants.

The cylindrical samples of titanium alloy, shown in Fig. 8, are subjected to tensile testing in order to determine the tensile strength in the certified Laboratory for Analysis and Testing of Materials and Calibration of Measuring Instruments (LIMC) at Institute of Metal Science, Equipment and Technology with Hydroaerodynamic Center, Bulgarian Academy of Sciences. The tests were performed according to the current standard BDS EN ISO 6892-1: 2009. The test results are presented in Table 1. The tensile strength of uncovered sample – 901.97 MPa, coincides with that of the coated ones, respectively – 901.93 MPa. The tests were performed at room temperature 20.0 ± 0.4°C. The results of the tensile tests show values for the mechanical characteristics, which are in accordance with the requirements of the standard for metal implants made of titanium alloys. A significant difference was observed only when determining the percentage of elongation after fracture, which is 27.1 MPa for uncovered samples and 34.4 MPa for covered samples, thus being 20% higher than.

Table 1: Mechanical properties of Ti6Al4V resulted from tensile testing ISO 6892-1:2019 (E)

Samples	Tensile strength, Rm [MPa]	Proof strength, plastic extension, Rp [MPa]	Percentage elongation after fracture, A [%]	Percentage reduction of area, Z [%]
uncovered	901.97	893.44	27.1	50.09
covered	901.93	894.98	34.4	52.23

Tests for determining the hardness and modulus of elasticity of the coating and the titanium substrate were performed using the prepared titanium alloy punch-shape samples shown in Fig. 1. In order to minimize the influence of the substrate on the determined hardness and modulus of the coating, the hardness and elastic (Young's modulus) modulus determination has been performed by nano-indentation or instrumented indentation technique. Nano-indentation is a reliable method for mechanical tests of materials in small volumes and shallow depths, which significantly expands the capabilities of traditional hardness tests. The device used is with continuous control and monitoring of the loads and movements of the indenter, from its penetration into the material to its withdrawal. This method gives the possibility for simultaneous determination of the applied load and the depth of penetration. Modern nano-indenters provide high accuracy and reliable results. Usually the load resolution is 1 nN, and the measurement accuracy for displacement is 0.1 nm. The maximal load varies, but for standard devices is up to 500 nN. An important advantage of nano-indentation is that the resulting load-displacement curve can be used to determine the elastic properties of the material. In addition, when determining the hardness of the material, there is no need to visually measure the imprint, as in conventional hardness test, thus avoiding introducing significant error in the result, especially for softer materials or coatings, where the imprint is deformed and accurate imprint size measurement is difficult. The fact that nano-indentation does not measure the geometric characteristics of the imprint, but uses the load-displacement curve, facilitates the determination of mechanical properties on a very small scale. Mechanical characteristics can be determined from an imprint with a maximum geometric size of less than 1 micrometer and a penetration depth of the indenter of only a few tens of nanometers.

This makes nanoindentation especially suitable for mechanical characterization of thin films and coating [10–13].

The mechanical properties are obtained from the indentation "load–displacement" curve, representing a graphical relationship between the applied load and the movement of the indenter relative to the level of the sample surface. From this curve, with the help of analytical functions, different mechanical characteristics of the test material can be derived, such as indentation hardness (HIT), indentation modulus (EIT), characteristics of the creep process and dependence of the deformation behavior on the load speed and others.

Figures 9(a) and (b) show the locations of 25 nano-indentations made on uncovered and glassy carbon covered punch-shape samples.

The results of the nano-indentation tests for determining the hardness and the elastic modulus were obtained in the Laboratory for 3D Digitalization and Microstructure Analysis and the Laboratory for Nanostructure Characterization at the Bulgarian Academy of Sciences. The results are presented in Figs. 10 and 11.

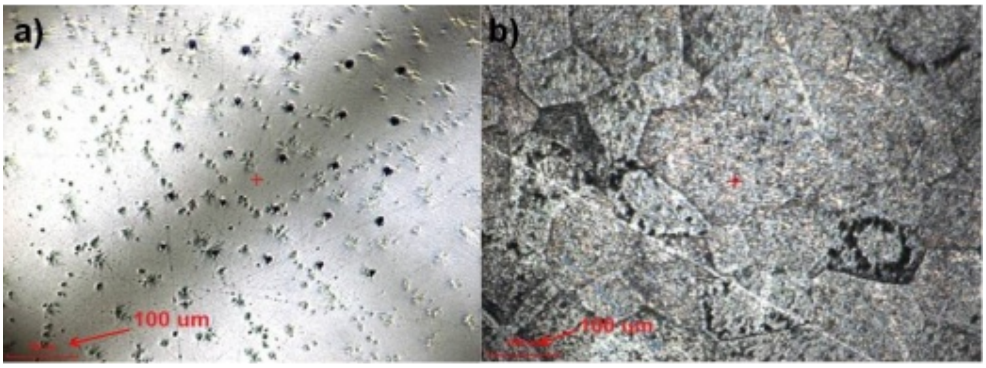

Fig. 9: Image of the nanoindentation testing locations with Nanoindenter G200: (a) Uncovered titanium sample; (b) Covered with glassy carbon titanium sample.

For the uncovered titanium alloy (Ti) the indentation hardness is about 5 GPa, a value very close to the results obtained by measuring the hardness by another method shown in Fig. 3, which is about 5.4 GPa. The indentation hardness of the glassy carbon layer (GC) deposited on the titanium alloy is about 11 GPa, an increase of about twice than the hardness of the uncovered titanium sample. On the other hand, the obtained result for the micro-hardness measured close to the one-micron glassy carbon layer shown in Fig. 3 is 2.4 GPa. It is a proof that the measured micro-hardness pre-

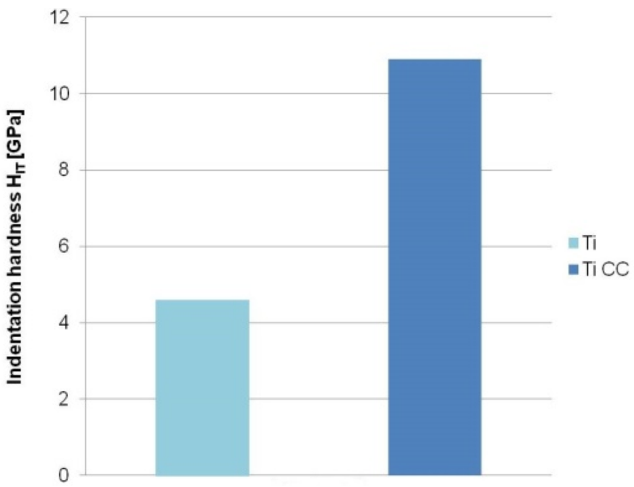

Fig. 10: Results of indentation hardness measurements of uncovered sample (Ti) and covered samples (TiGC).

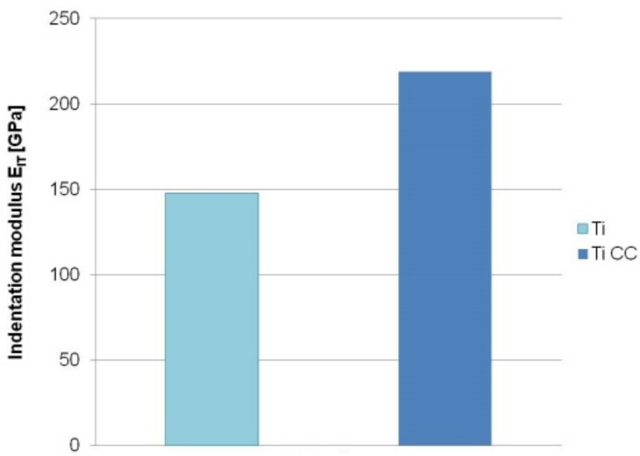

Fig. 11: Results from the elastic modulus measurements for uncovered sample (Ti) and covered sample (TiGC).

sented in Fig. 3 is significantly influenced by the properties of the titanium substrate, because the diamond pyramid, has a larger imprint than the thickness of the studied layer.

The elastic modulus of uncovered and covered samples was determined and the results are shown in Fig. 10. For titanium alloy (Ti) the elastic modulus is about 150 GPa, and for titanium alloy covered with glassy carbon (TiGC) it is about 215 GPa. The increase in the modulus of elasticity of the covered samples is most likely due to phase or structural changes in the titanium alloy as a result of the heat treatment used during thermo-chemical deposition procedure for obtaining the glassy carbon coating. To note, there are two polymorphic modifications of titanium: up to 882°C it is in the form of α-modification, which has a hexagonal dense packing of the crystal lattice with parameters $a = 2.95$ Å and $c = 4.86$ Å and above this temperature, the β-transformation with volume-centered cubic lattice ($a = 3.31$ Å) [14].

3 Conclusions

A new composite biomaterial consisting of bio-titanium alloy and bio-glassy carbon coating was obtained by novel original technology. As outcome, the durability of the implants can be increased. The major conclusions about the superior features of the proposed biocompatible composite material are:

- The percentage of elongation after fracture of the titanium alloy covered with glassy carbon is 20% higher than in the case of uncovered titanium alloy.

- The hardness of covered with glassy carbon titanium alloy is twice as high as that of the titanium alloy.
- The modulus of elasticity of the covered with glassy carbon titanium alloy is almost 40% higher compared to that of the uncovered titanium alloy.

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