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Partial Oxidation of Biocompatible Titanium Alloy Ti 6Al 4V During Deposition of Glassy Carbon Coating

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Abstract
The deposition of glassy carbon coating on titanium alloys is performed thermochemically. This combination of biocompatible coating and biocompatible titanium substrate is an innovative implant composite for application in medical care. The objective of this study is to determine the reason of the partial oxidation of titanium substrates during the deposition of glassy carbon. The deposition of glassy carbon is usually carried out in vacuum or in protective environment, most often in Ar, at temperatures around 1000oC. The changes of the phases in the direction of the flow of the protective gas in the temperature zone of the furnace were studied by XRD analysis.

Keywords: titanium alloys, glassy carbon, coating, biocompatible, oxidation

1. Introduction

The main research task is to create a composite consisting of a biocompatible titanium alloy coated with a biocompatible glass-carbon coating. The deposition of glassy carbon (GC) on the titanium substrate is carried out thermo chemically. Plasma porous titanium is preliminarily deposited on the titanium alloy [1]. Meanwhile, titanium-based porous alloys are being intensively developed as an alternative material for orthopedic implants, as they can provide good biological fixation by increasing bone tissue in the porous network.[2] In principle, the main requirements for the characteristics of implant materials are: low elastic modulus, high strength, excellent resistance to corrosion and wear, good biocompatibility. Of the metallic materials, titanium and its alloys are considered the most suitable products for biomedical applications because of their properties meeting the requirements for implantation, according to world standards. They perform better overall than other competing materials, such as various stainless steels, cobalt alloys, pure niobium and tantalum metals.
Glassy carbon is obtained by heat treatment by decomposition of polyvinyl chloride (PVC) at 380°C, resulting in a powdered product from which hydrocarbon solutions (CnHn)n are prepared.[3] Glassy carbon, as a newly formed glassy form of carbon, is characterized by: high chemical purity, high corrosion resistance, impermeability to gases and liquids, high hardness – almost like that of ceramics, low density, very good surface polishing properties, very good resistance to thermal shocks, good electrical conductivity, biocompatibility, isotropy of physical and chemical properties. Another important advantage of glassy carbon materials is that their physical properties are close to those of bone. For example, their relative weight, according to the type of carbon, is in the range of 1.5 – 2.2 g/cm^3, and their modulus of elasticity is between 4 – 35 GPa. Table 1 compares the properties of glassy carbon and human bone [4]. The Young's modulus of the cortical bone is 11–21 GPa longitudinally and 5–13 GPa transversely. Our bones are amazing in compression, with compressive strength ranging from 70-280 MPa. The resistance of the bone to fracture has an impressive value of 1.5 kJ/m^2. In comparison, most trees have a breaking strength of only 70-120 J/m^2 [5].

Table 1. Properties of glassy carbon and human bone

Material	Young's Modulus GPa	Compressive Strength MPa	Bond strength GPa	Hardness	Density g/cm^3
Vitreous Carbon	24-31	172	70-207	150-200 (DPH)	1.4-1.6
Bone	3-30	130-180	60-160	NA	NA

The studied titanium samples are in the form of square tiles with dimensions – 30 x 30 mm, h – 2.5 mm. A plasma layer of porous titanium is deposited on them for better integration of the implant with the bone. The first deposition of titanium substrates with glassy carbon is performed at a temperature of 1350°C in order to obtain intermediate TiC layer for a better adhesion of the glassy carbon to the titanium matrix. The next deposition is performed at temperatures of 950 – 1000ºC. This thermochemical process is repeated many times until a certain thickness of the glassy carbon layer is reached, most often about 10 µm.

2. Results and discussion

Figure 1 shows the microstructure of a glassy carbon coating deposited on a porous layer titanium alloy in a 99.996% purity argon protective medium. The coating is black and glossy, relatively even and continuous. Figure 1a shows a section of a glassy carbon coating deposited on a titanium matrix with porous titanium. It is clearly observed that the glassy carbon layer follows the surface of the porous titanium matrix. It has a roughness of about 50 µm (Fig. 1a), where a partial filling of the porous. The first thermo chemical process was carried out at temperatures around 1350°C in a tube furnace (Fig.2) in a stream of technical Ar with a purity (99.996%). It is one of the most important processes preceding the actual deposition of glassy carbon at 950°C on the porous titanium matrix. In this primary high-temperature process, titanium carbide is partially synthesized, acting as a bond between the titanium matrix and the glassy carbon coating.

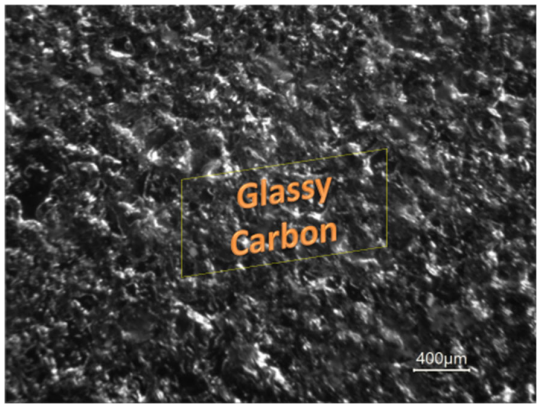

Figure 1. Micro image of GC coating on titanium sample – x400

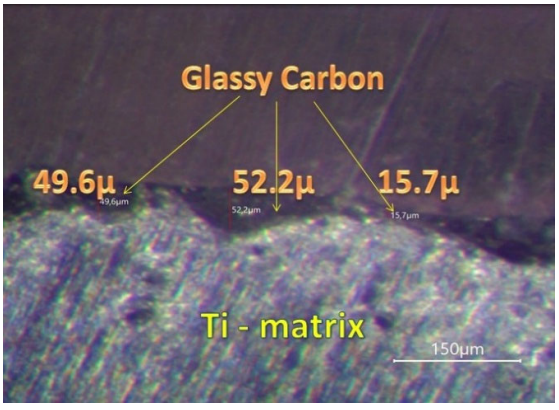

Figure 1a. Microstructure of GC coating on titanium substrate with porous titanium

The glassy carbon coating shown in (Fig.1a) is continuous with good adhesion, relatively uniform on the porous titanium surface, with a thickness of not less than 10 µm.

Fig.2. Tube furnace for thermo-chemical deposition of glassy carbon

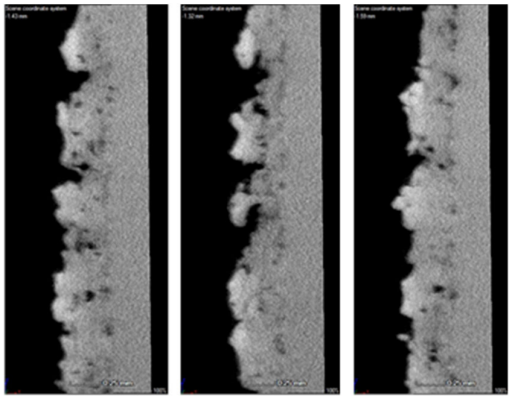

Figure 3. 3D image of the surface of porous titanium coated with glassy carbon along the xz axis

Computed tomography images of 3D images of porous titanium with GC deposited on it are shown in Fig. 3–4) along the xz and yz axes. Partial filling (flooding) of the pores with glassy carbon on the porous titanium structure was observed in different sections of the entire sample surface. Figure 5 shows partially oxidized samples from Ti1 to Ti5 in the direction of the incoming argon protective gas without the use of protective titanium chips. They need to be placed at the inlet of the furnace to absorb any possible contamination of the argon with air and water vapor leading to partial oxidation of the titanium samples with glassy carbon.

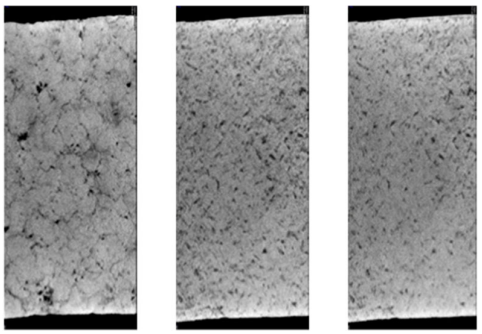

Figure 4. 3D image of the surface of porous titanium coated with glassy carbon along the yz axis

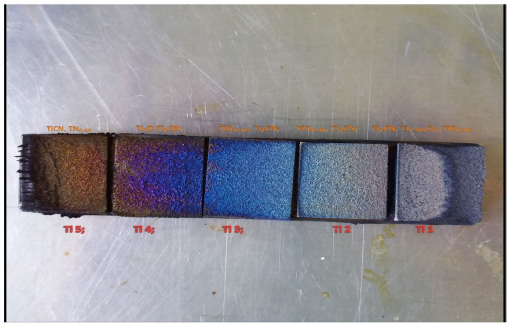

Figure 5. Image of partial oxidation of the surface of titanium samples coated with glassy carbon at 1350°C

Figure 6. Image of the partial oxidation of protective titanium chips

Diffraction studies were performed with a Siemens D500 diffractometer with a copper anode (λ = 0.154 nm) at monochrome radiation. X-ray analyzes were performed using 2θ from 15 ° to 85 °. X-ray diffraction studies of Ti 64 samples with porous titanium coated with glassy carbon were performed. Depending on the heating zone and the flow of protective gas (Ar), different phases with the corresponding color were obtained (Fig. 5). A similar coloration is observed on the protective titanium chips placed at the inlet of the furnace where the Arprotective gas passes (Fig. 6).

An X-ray technique (Bragg-Brentano) was used to analyze the samples. The diffractograms of five titanium samples (Ti1, Ti2, Ti3, Ti4, Ti5) and the main phases obtained from partial oxidation at deposition of glassy carbon on titanium porous substrates at temperature of 1350^0C are shown (Fig. 7-11). The direction of the incoming argon protective gas is from sample Ti1 to sample Ti5 and in the same direction the oxidation of the samples was reduced. In sample Ti1, three phases were registered in descending order of their amounts: Ti_2CN (dititanium carbonitride), $Ti_{0.924}O_2$, (non-stoichiometric titanium dioxide) and $TiO_{0.48}$ (non-stoichiometric titanium oxide) (Fig. 7). In the Ti2 sample, two phases were registered: more Ti_2CN (dititanium carbonitride) and less $TiO_{0.48}$ (non-stoichiometric titanium oxide) (Fig. 8). Two phases were registered in the Ti3 sample: $TiO_{0.325}$ (non-stoichiometric titanium oxide) and Ti_2CN (dititanium carbonitride) (Fig. 9). In the next diffraction pattern of sample Ti4, two phases were found: Ti_3O (trititanium oxide) and Ti_2CN (dititanium carbonitride) (Fig. 10). Two phases were found in the last sample Ti5: $TiC_{0.496}N_{0.502}$ (non-stoichiometric titanium carbide nitride) and $TN_{0.30}$ (non-stoichiometric titanium nitride) (Fig. 11).

The oxidation decreases from sample Ti1 towards the inside of the furnace to Ti2, Ti3 and Ti4 and there is no oxide phase in sample Ti5.

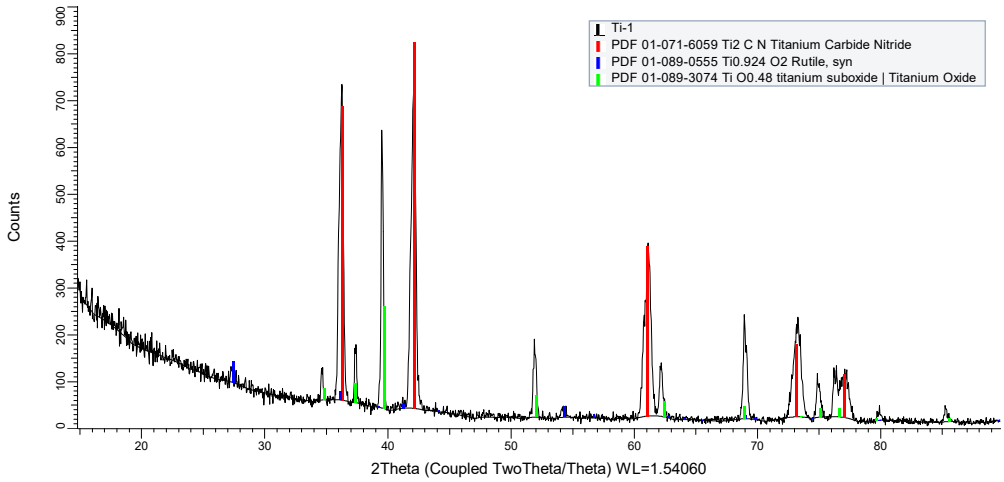

Figure 7. Diffraction pattern of sample Ti1 partially oxidized at 1350°C

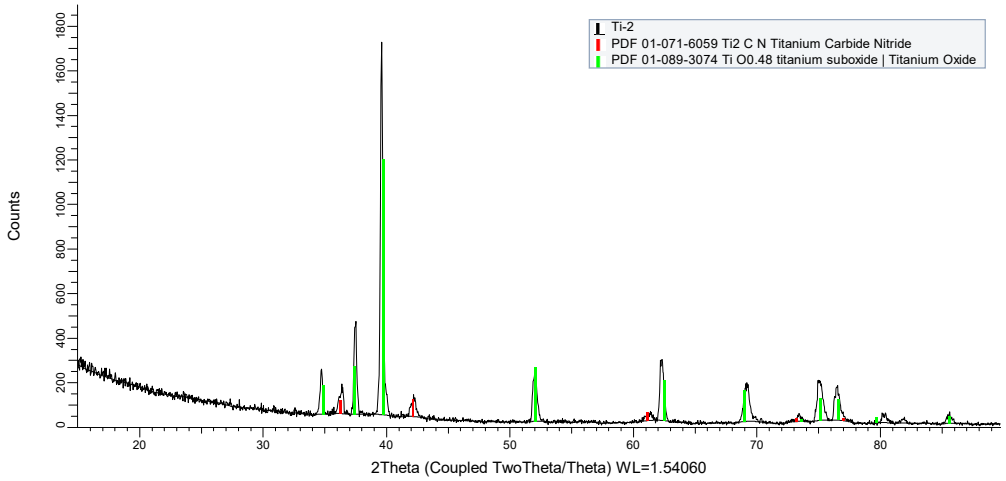

Figure 8. Diffraction pattern of sample Ti2 partially oxidized at 1350°C

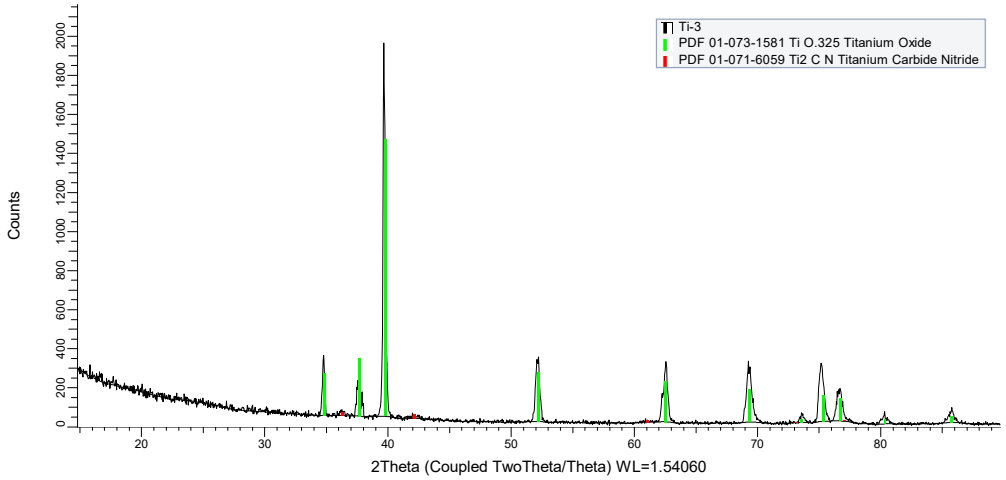

Figure 9. Diffraction pattern of sample Ti3 partially oxidized at 1350°C

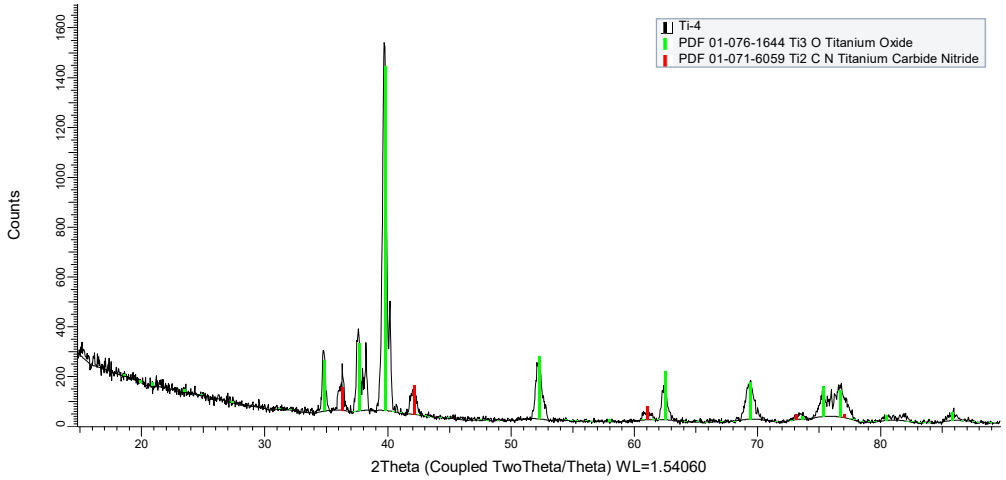

Figure 10. Diffraction pattern of sample Ti4 partially oxidized at 1350°C

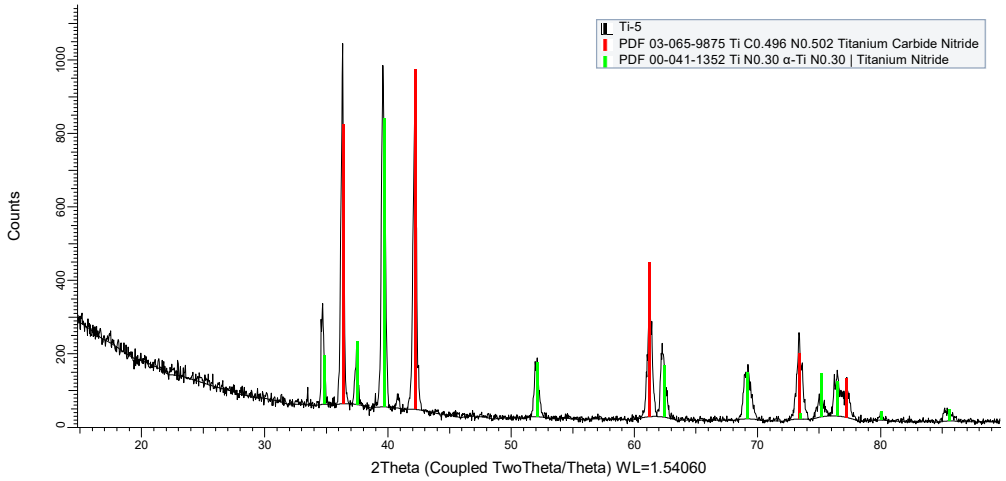

Figure 11. Diffraction pattern of sample Ti5 partially oxidized at 1350°C

3. Conclusions

- It was found that the use of pressure vessel with technical Ar below 50 at. contributes to partial oxidation in the primary deposition of glassy carbon on Ti 64
- It has been proven that without titanium chips at the inlet of the furnace, from where the protective argon gas is supplied, the titanium samples with glassy carbon are partially oxidized.
- It has been found by XRD that the oxidation of titanium decreases in the direction of the inside of the furnace and the phase composition goes from non-stoichiometric titanium oxynitrides, then carbonitrides and finally to oxygen-free titanium carbonitrides.

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