GLASS- CARBON BIOACTIVE COATINGS ON A TiO_2- Nb_2O_5 SUBSTRATE

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ABSTRACT

The research carried out studies the processes of coating and impregnation of non-active glass carbon coatings on TiO_2-Nb_2O_5 substrates, intended for surgery implants for hip joint prostheses. It was found that the coating procedure implemented and the subsequent impregnation, lead to filling of the substrate' pores with glass carbon, thus resulting in a substantial decrease of the substrate's roughness. It was found that preliminary treatment of the substrate aiming at a formation of TiC on its surface is important for the subsequent buildup of a stable glass-carbon coating. The tribological measurements carried out show substantial decrease of the friction coefficient of vitreous carbon (VC) – hip joint, which is the prerequisite for using these coatings as surgery implants for hip joint prostheses.

KEYWORDS: Titanium ceramics, bioactive coating

1. Introduction

The usage of ceramics for biomedical technical applications has gained considerable momentum since the end for 1960. The bioceramic materials were used initially as alternative of the metal implant materials, aiming at the improvement of the biological compatibility implant- human tissue. Since then they have developed in an independent class of biomaterials widely used nowadays at their own right as tissue - bone, implants.

Some inert bioceramics of the Al_2O_3, ZrO_2 type, showed excellent tribological properties and stability towards skin-deep traumas, when used as endoprostheses, mainly in the production of heads for pelvic thigh anchylosises.

The alumina ceramics Al_2O_3 have been used in the world orthopedic practice, as well in Bulgaria, for more than 30 years.

The clinical results from this period demonstrated that the wearing out between the head from alumina ceramics and the cup from polyethylene [1-8] is negligible making it an excellent material for bone implants. However, the usage of ceramics as implants is not without problems.

Due to their insufficient mechanical strength, risks of a sudden breakage could not be eliminated.

Another, still unsolved problem, concerning the materials used for heads of pelvic thigh anchylosis, is their limited life span, which is an issue of crucial importance, especially when these are implanted in young patients. Therefore, a sharp increase of their service life say up to 20 years is highly desirable.

To address the challenges above, in the BAS, a new inert bioceramic material, based on the oxide ceramics TiO_2 (Rutile) - Nb_2O_5, was developed and since then intensively investigated [9-13].

The concept behind the development of the new biocompatible composite ceramic material, based on TiO_2 (Rutile) and Nb_2O_5 with additions of nano-carbon ingredients, is that the vitreous carbon covers the ceramic substrate surface more effectively. Thus, a target surface roughness of the coated substrate down to 3 microns could be reached.

Moreover, a coating consisting entirely of carbon will not be rejected from the organism of the patient.

The method developed for synthesis of this new ceramic material is based on the assumption that during the thermal treatment, the titanium dioxide ceramic and the deposited carbon glass coating will

react and form a thin layer of titanium carbide in the ceramic-coating interface.

It is assumed, that part of the carbon will be consumed for reduction of the titanium dioxide lying near the interface, and that another part will participate in building of transitional carbide layers filling the pores of the ceramic body. The transitional carbide layer would also serve as anchor of the glass-carbon layer, thus reducing risk of breakage between the ceramics and the coating. It is expected that a coating of carbon glass produced by thermal deposition, would have very high rank of roughness, thus eliminating the necessity of end polishing of the friction surfaces.

The aim of the present paper is a study of newly developed biocompatible composite ceramic material, based on TiO_2 (Rutile) - Nb_2O_5 ceramic with additions of nano-carbon ingredients, intended for production of endoprotheses.

2. Experimental procedure

2.1. Synthesis of the ceramic substrate TiO_2 - Nb_2O_5

The ceramic substrate specimens studied were prepared by mixing TiO_2 and Nb_2O_5 powders in proportions ensuring concentration of 8 wt.%. Nb_2O_5 in the final product. The choice of Rutile as base powder of the mixture is due to its structure. The Ti atoms in the Rutile (TiO_2) occupy the centre of a slightly deformed octahedron formed by the Oxygen atoms. This positioning of the Rutile's atoms determines its great capacity to incorporate in its lattice donor elements, or donor ions.

Because the Nb^{5+} ion radius of the Nb_2O_5 substance is commeasurable with the Ti^{4+} radius (RTi^{4+} = 0,69 A, RNb^{5+} = 0,70 A) it is easily embedded into the Rutile cell's voids, resulting in negligible change of the Rutile lattice parameters. Thus, when Nb_2O_5 is added in small quantities it would not deform the Rutile lattice and the mechanical properties of TiO_2 ceramic would be preserved [14-15].

The concrete ceramic synthesis procedure used, is as follows: firstly, the mixture is granulated and then under isostatic pressure it is formed into the desired form of the substrate.

The substrate specimens prepared for this study were with diameter of 35-36 mm and 10mm thick. The as prepared substrate specimens were sintered at temperature of 1450ºC according to a predetermined temperature regime.

The next step of the production of the coated ceramics is the generation of carbides on the substrates' surface. For this purpose the ceramic substrate, in our case the prepared TiO_2 - Nb_2O_5

sinter, is covered with polymer organic material, with complex structure of the type (CnHm). During the heating the polymer decomposes to: carbon, which subsequently forms the desired carbide structure; H_2 and organic radicals (CxHy).

The presence of H_2 in the furnace atmosphere favours the reduction of the oxides at the ceramic's surface, by extracting and chemically bonding the labile Oxygen O^{2+} ions. The freed chemical bonds are later saturated by the carbon atoms obtained by the decomposition, thus, forming the desirable carbide layer on the substrate surface.

Obviously, the temperature regime of heating and the thickness of the polymer coating are crucial for obtaining a quality carbide layer. For this purpose the "heat-hold-cool" regime was selected after modeling and numerous trial-error experiments. It was found that most favorable for the formation of the desirable structure of the substrate is heating with 10K/min up to 1450ºC in inert gas atmosphere with subsequent cooling with approximately the same cooling rate.

The processes, taking place during the carbide layer production, were constantly monitored using sophisticated thermal analysis apparatus, Setaram **DTA-TG-MS LABSYS-evo**. Powder X-ray diffraction (XRD) patterns for characterization of the samples were collected at room temperature on a **Bruker D8 Advance** diffractometer using CuKα radiation and Sol-X detector.

The measurement range was from 10º to 80º 2θ with a step of 0.04º 2θ and 1 s/step counting time. Phase analysis of the powder patterns was done using EVA v.12 program and ICDD PDF-2 database, 2006-release.

2.2. Coating of the substrate specimens

This is the last stage of production of glass carbon coated bioceramics.

As mentioned, it is done to improve the mechanical and the tribological quality of the final product, TiO_2-Nb_2O_5, and as well for the ceramic's compatibility with the human tissue.

The procedure itself is as follows: firstly, the specimens are saturated in organic solution of polymer hydrocarbons with controlled concentration.

The process of preparation and degradation of the polymer used are described in details in the *Appendix*; secondly the specimens are dried in vacuum at 150ºC; lastly the specimens are heat treated at 1000-1100°C in inert gas atmosphere using an empirically selected temperature regime, which is: heating of 15 to 20 °C/min.; holding at 1000-1100°C for 30-50 min. and cooling to room temperature.

This procedure is repeated several times until the desirable roughness grade and layer thickness is reached.

3. Results and discussion

3.1 X-ray phase analysis and SEM results

Before coating, the structure of the as sintered specimens, has been studied with X-ray and SEM analyses. The results obtained are shown in Figs.1 and 2. The X-ray analysis showed, as expected, that the crystal reflection planes after combined sintering of the TiO_2 and Nb_2O_5 powders are changed, which is evinced by a shift of the reflects observed, to a smaller reflecting angles. As known, this is a result of the distance increase between the crystal reflection planes due to the formation of a compound formed by the interaction between TiO_2 and Nb_2O_5 powders.

It our particular case, the compound formed has a crystal lattice, of the type $(Ti^{4+}_{1-2x} Nb^{5+}_x Ti^{3+}_x)O_{2-x}$.
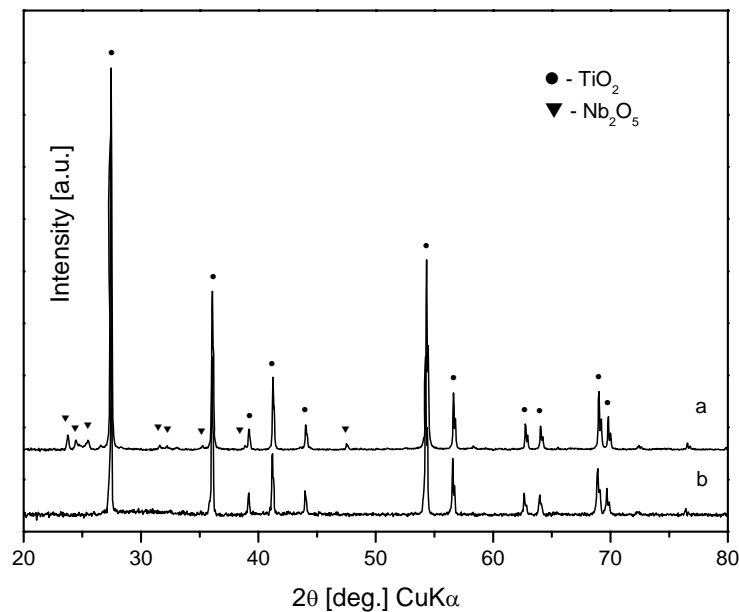

Fig. 1. *X-ray phase analysis of Rutile TiO_2 – Nb_2O_5 ceramics.*

The formation of this compound results from the charge conservation law, where one of Ti^{3+} for every Nb^{5+} is reduced, thus keeping the mean charge of 4^+ for every Ti atom preserved. The microstructure of the sintered substrates was studied by SEM.

The micrographs obtained are shown in Fig.2.

As seen, the structure of the ceramic substrate is characterized by oval voids measuring 3-4 µm and isometric grains measuring up to 20 µm.

This type of microstructure with strongly developed surface was intendedly pursued and is very favorable for obtaining strong bonds between the VC coating and the carbide layers of the ceramic matrix. The experiments carried out, showed that part of the Nb_2O_5 reduces to NbO_2, during the sintering, which gives a characteristic bluish black colour of the sinter. It should be noted, that this transformation does not affect the mechanical or chemical properties of the substrate.
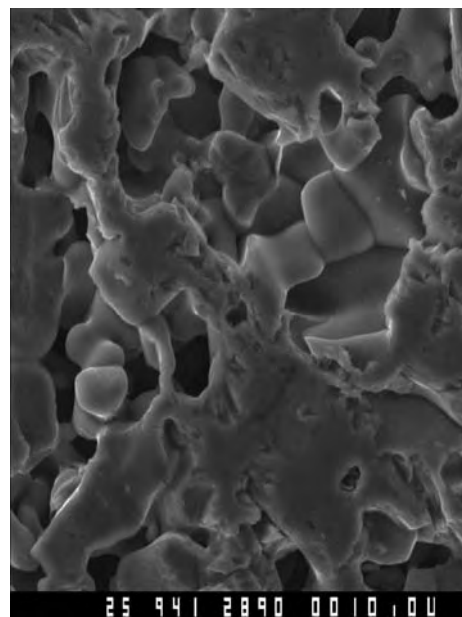

Fig. 2. *SEM image of TiO_2-Nb_2O_5, specimen. x940*

3.2 Thermo-gravimetric experiments

Fig. 3 shows the results obtained by the thermo -gravimetric analysis of the specimens prepared from granulated TiO_2-Nb_2O_5.
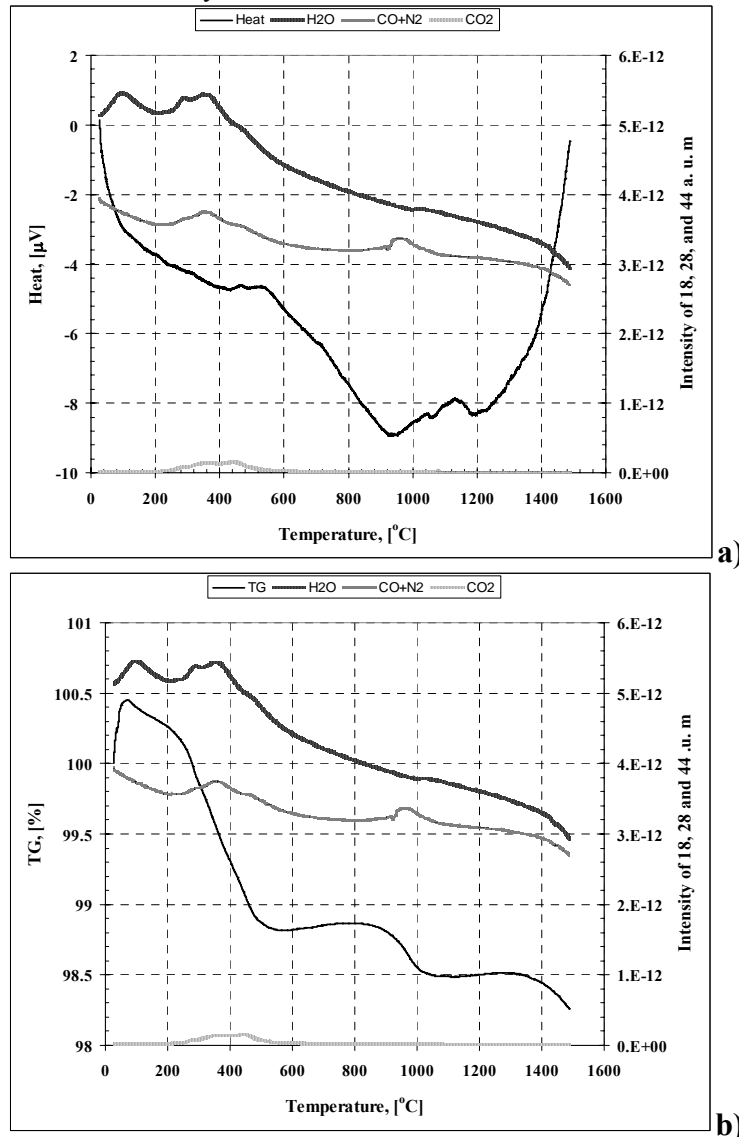

Fig.3a *and* **3b**. *DTA and gravimetric curves obtained during the precursory treatment of the ceramic substrate surface with carbon aiming at the development of TiC on the substrate surface.*

The gravimetric results show that the first stage at the sintering of the specimens is the evaporation of the residual moisture followed by degradation of the PVC used. This process continues up to 600ºC and is characterized by a considerable weight decrease of the specimen. The sintering itself takes place in the temperature interval 850-1200ºC. At this stage the weight still decreases but it is not so intensive compared to the first stage. It was concluded that this is due to the reduction of the oxides forming the substrate. At the end of this stage two characteristic endothermic peaks are observed on the DTA curve, due to the formation of carbides on the substrates' surface. It should be reminded, that the formation of

carbides is of crucial importance for the mechanical strength of the final VC coating. The DTA-gravimetric experiments carried out, were crucial for the determination of the optimal temperature regime of sintering. Analyzing the results obtained at different temperature regimes, the following optimal regime of sintering was selected: heating rate of 5ºC/min. from room temperature to 600ºC; heating rate of 10ºC/min. from 600ºC to 1450ºC and holding at temperature of 1450ºC for 45 to 60 min. The lower heating rates at the beginning are to avoid the distortion and the subsequent crumbling of the specimen, due to intensive separation of moisture and hydrocarbon radicals.

3.3. Tribological experiments. The friction coefficient

The coefficient of friction (CoF), symbolized below by the Greek letter μ, is a dimensionless scalar value which describes the ratio of the force of friction F between two bodies and the force pressing them together N (the normal force): $\mu = F/N$. It should be noted that the friction coefficient is velocity sensitive, i.e. its value depends on the velocity between the friction surfaces.

The results reported here are obtained from measurements of the friction coefficient between coated with vitreous carbon (VC) and not coated ceramic specimens of TiO_2-Nb_2O_5 with substrate of low molecular polyamide, used for production of acetabular capsules at endoprosthesing.

Table 1

№	Nomenclature	Without coating		After coating with VC	
		Initial friction coefficient, μ_0	Dynamic friction coefficient, μ	Initial friction coefficient, μ_0	Dynamic friction coefficient, μ
1.	П	0.14	0.11	-	-
2.	600/07.10.2009	0.22	0.12	-	-
3.	2.15-400	0.25	0.16	0.14	0.09
4.	2.16-400-1	0.22	0.16	-	-
5.	2.17-220	0.26	0.14	-	-
6.	3.15	0.22	0.15	-	-
7.	3.16	0.40	0.28	0.24	0.17
8.	3.19	0.38	0.32	-	-
9.	4.15-400	0.20	0.14	-	-
10.	4.16-П	0.12	0.08	-	-
11.	4.17-200	0.24	0.14	-	-
12.	4.18-400-1	0.21	0.12	-	-
13.	4.19-600	0.16	0.11	-	-

The experiments were carried on cylindrical specimens at N=50 –150 N and velocities of 10 – 300 mm/s.

Two values of CoF were measured: the Initial friction coefficient, μ_0, where the specimens are stationary in respect to the substrate and dynamic friction coefficient, μ, for moving specimens.

The results obtained are summarized in Table 1.

The results presented show that the specimens coated with VC have smaller static and dynamic CoF compared to the not coated ones. It is worth noting, that the higher values of μ_0 compared to μ, are due to several factors, such as the material's nature, the material's physical condition and its roughness.

3.4 Microstructure-roughness measurements

As part of the material characterization, the roughnesses of the specimens before and after coating with VC were also measured, using profile meter **Rugosurf 10G**.

The results obtained are summarized in Table 2.

The measurements were carried out at a base length of 0.25 mm and averaging of 5 base lengths. The mean deviation of the profile from the mean line R_a and the roughness height R_z obtained as a mean of the highest and lowest points within the base length were determined.

The results of the measurements microstructure roughness for the specimens studied are summarized in Table 2.

The results obtained show that the mean deviation of the profile R_a of the studied specimens varies within the 0.47 – 1.00 μm range, the R_z is within the limits of 3.00 – 6.00 μm, except for the specimens #4 and #8. It is obvious that VC reduces the roughness of the ceramics' surfaces, which is a prerequisite for using coated ceramics for surgery implants at hip joint prosthesing.

Table 2

№	Nomenclature	Without coating		After coating with VC	
		R_a, μm	R_z, μm	R_a, μm	R_z, μm
	П	0.685	4.574	-	-
	600/07.10.2009	0.630	3.911	-	-
	2.15-400	0.959	4.910	0.612	3.98
	2.16-400-1	1.454	8.430	-	-
	2.17-220	1.020	5.742	-	-
	3.15	0.471	3.432	-	-
	3.16	0.485	3.053	0.363	2.646
	3.19	2.914	14.344	-	-
	4.15-400	0.834	5.086	-	-
	4.16-П	0.605	3.907	-	-
	4.17-200	0.884	5.156	-	-
	4.18-400-1	0.734	4.860	-	-
	4.19-600	0.709	4.082	-	-

4. Conclusion

The processes of coating and impregnation of non-active glass carbon coatings on TiO_2-Nb_2O_5 substrates, produced by sintering and intended for surgery implants for hip joint prostheses, were studied. It was found that a precursory development of TiC on the substrate surface, facilitates the subsequent buildup of a stable glass-carbon coating. A temperature regime for the coating procedure using modeling and trial-error experiments was determined and implemented.

The tribological measurements carried on ceramic specimens, coated with the method described, show substantial decrease of the friction coefficient glass carbon – hip joint, which is the prerequisite for using these coatings as surgery implants for hip joint prostheses.

Appendix

The PVC degradation

The precursor for glassy carbon coating was produced by thermal decomposition of PVC. The PVC used shows two stages of degradation. During the first stage, which is between 200 and 360°C, mainly HCl, benzene, and very little alkyl aromatic or condensed ring aromatic hydrocarbons are formed. About 15% of the polyene generates benzene, the main part accumulating in the polymer and being active in intermolecular and intramolecular condensation reactions, by which cyclohexene and cyclohexadiene rings embedded in an aliphatic matrix are formed.

Alkyl aromatic and condensed ring aromatic hydrocarbons are formed in the second stage of degradation, between 360 and 500°C, when very little HCl and benzene are formed. In this stage the polymeric network formed by polyene condensation breaks down in the process of aromatization of the above C rings.

In the specific research the PVC degradation was carried out at 380°C, temperature with a heating rate of 5°C/min and soak time at the final temperature for one hour. This allows completely eliminate the Cl as HCl and is obtained a final product with appropriate composition for formation of stable coating of classy carbon on the TiO_2-Nb_2O_5 substrate surface.

Acknowledgements

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