A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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# PRELIMINARY CHARACTERISTIC OF COMPOSITE COATINGS C/HAp PRODUCED RESPECTIVELY BY RF PACVD AND SOL–GEL METHODS

# WSTĘPNA CHARAKTERYSTYKA KOMPOZYTOWYCH POWŁOK C/HAp WYTWORZONYCH ODPOWIEDNIO METODAMI RF PACVD ORAZ ZOL–ŻEL

The required high mechanical strength and the reliability of implants on one side and a lack of toxic elements in those materials, on the other side, causes restrictions in use of metal alloys for austenitic steel, alloys of cobalt matrix and even titanium alloys. However, elements harmful to human body structure such as chromium, nickel and vanadium could not have been eliminated so far. An attempt to reduce detrimental effects of above elements on the living organism are surface modifications of materials predicted for implants through the deposition of protective layers.

The C/HAp composite coating was prerared by deposition of carbon layer directly on surgical steel with RF PACVD method and manufacturing of hydroxyapatite layer by sol-gel method. It was proved that carbon film significantly increases adhesion of the composite C/HAp coating. It is due to the diffusive character of bonding between carbon layer and metallic substrate not only by adhesion as in the case with hydroxyapatite deposited directly on metal base. Adhesion of both synthesized coatings was determined using nanoindentation technique. X-Ray diffraction was used for phase composition evaluation. Atomic Force Microscope revealed topography of raw, carbon and C/HAp surfaces. Elemental composition of carbon and composite layers was investigated by scanning electron microscope equipped with x-ray energy dispersive spectroscopy detector.

*Keywords*: hydroxyapatite, sol-gel, adhesion, carbon, implant

Wymagana wysoka wytrzymałość mechaniczna i niezawodność implantów z jednej strony i nie stosowanie w materiałach pierwiastków toksycznych (alergizujących) z drugiej strony, powoduje ograniczenia w stosowaniu stopów metalicznych, przeznaczonych na implanty, do stali austenitycznej, stopów na osnowie kobaltu i stopów tytanu. Mimo starań, nie udało się jednak z materiałów tych całkowicie wyeliminować pierwiatków szkodliwych dla organizmu jak choćby chromu, niklu i wanadu. Próbą ograniczenia złego wpływu pierwiastków na żywy organizm są modyfikacje powierzchni materiałów przeznaczonych na implanty poprzez wytwarzanie na nich warstw ochronnych.

Kompozytowa powłoka węgiel/hydroxyapatyt została otrzymana przez naniesienie w pierwszej kolejności warstwy węglowej bezpośrednio na stal AISI 316L metodą RF PACVD a następnie warstwy hydroxyapatytu metodą zol-żel. Zostało udowodnione, że warstwa węglowa w sposób znaczący zwiększa adhezję kompozytu C/HAp do zastosowanego podłoża. Jest to wynikiem dyfuzyjnego charakteru połączenia pomiędzy warstwą węglową a podłożem a nie jak w przypadku bezpośredniego naniesienia powłoki HAp na podłoże gdzie połączenie takie ma charakter adhezyjny.

Adhezja obu wytworzonych powłok (C, C/HAp) została określona po użyciu nanoindentera F-MY MTS Instruments Nano G-200 metodą *scratch test*. Analizę składu fazowego podłoża oraz uzyskanej powłoki kompozytowej dokonano metodą dyfrakcji rentgenowskiej. Badania topografii powierzchni z wytworzonymi warstwami węglową oraz węglowo/hydroxyapatytową przeprowadzono przy użyciu mikroskopu sił atomowych (AFM) F-my Veeco Multimode z kontrolerem NanoScoper. Chropowatość warstwy wierzchniej określono przy pomocy parametru $R_a$. Mikroanalizę rentgenowską wykonano przy pomocy przystawki Thermo-Noran zainstalowanej w mikroskopie scaningowym HITACHI S-3000N. Zastosowano technikę analizy liniowej (EDS).

## 1. Introduction

Special properties of austenitic steel, such as: good corrosion resistance in various environments, good strength parameters, easy plastic and thermal forming and a significantly lower price in comparison with titanium and cobalt alloys, favour its wide range of applications in manufacturing of short-term implants. However, it is practically impossible to use this steel for long-term implants due to toxicity. Thus, it is still one of the most important challenges to surface engineering to improve these deficient functional properties of this steel to enable its application in the manufacturing long-term implants. The relevant literature shows that it is possible to modify the surface of surgical steel in such a manner that the toxic influence on human body could be significantly limited. One of the possibilities is to produce carbon and hydroxyapatite layers

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on austenite steel. Carbon layers exhibit perfect bio-inertness in contact with the human body and at the same time they constitute a perfect barrier between metal ions and the tissue surrounding the implant [1÷4]. Biocompatibility of metal implants can be significantly increased by applying a thin hydroxyapatite coating onto the implant [5,6]. This material is characterized by the chemical and phase composition similar to the bone tissue [7,8]. That is why it is accepted by human immunological system. Hydroxyapatite ceramic is biologically active and among all types of ceramics has the highest biotolerance making hydroxyapatite materials easily resorped by human body. The main feature of HAp is its osteoinductivity which means the support of bone rebuilding processes. Synthetic hydroxyapatite in an environment of body fluids may undergo resorption.

At present, intensive research is being conducted on improving the adhesion of the hydroxyapatite coatings to the various metal substrates by choosing appropriate parameters of the manufacturing method but also by creating intermediate layers at the metal-HAp [9÷14]. At the same time, it must be emphasised that despite of intense research, no hydroxyapatite coating on surgical steel has been produced to date that would have adequate functional properties applicable for long-term medical implants.

An interesting solution that increases the adhesion of the HAp coating to the metal substrate can be the application of an intermediate carbon layer, which will also limit the penetration of metal ions into the tissue surrounding the implant. By combining the benefits of both methods of surface treatment, a new technology could be developed for manufacturing materials for long-term implants using surgical steel.

This paper presents a study on depositing composite C/HAp coatings on AISI 316L steel for medical purposes. Carbon layer was produced directly on surgical steel with the RF PACVD method and outer HAp layer was deposited with the sol-gel method. It was turned out that the carbon layer significantly increases adhesion of the composite C/HAp coating because it is bonded to the composite coating by diffusion and not only by adhesion, as is the case with hydroxyapatite.

## 2. Materials and methods

### 2.1. Preparation of coatings

The material used for the research was implant grade supersaturated AISI 316L steel disks (8mm in diameter, 5mm thick) whose chemical composition complied with the ISO 4967-19769E0 standard.

Carbon layer with an average thickness of 120 nm was deposited using the RF PACVD method described by Mitura [15]. The method is based on exciting plasma in methane with nitrogen in an RF electric field at high gas pressure.

Hydroxyapatite layers were prepared by the sol-gel method and deposited on AISI 316L steel samples as well as on the same substrates previously coated with carbon film. HAp sol was obtained from calcium nitrate and tri-ethyl phosphate which were dissolved in ethanol separately. After mixing, the as-prepared solution was aged at temperature of 60°C for 15 h. Samples were deposited by dip coating and rapidly heated at 500°C for 5 min. The HAp coating deposition procedure was repeated three times. Finally the coating was annealed at the temperature of 500°C for 20 min.

### 2.2. Characterization of coatings

Surface of the AISI 316 sample before and after deposition of carbon layer as well as the HAp crystalline structure was analysed with Simens D-500 X-ray diffractometer (XRD) using Co-K$\alpha$ characteristic radiation and graphite monochromator. The XRD diffraction patterns have been identified based on the ICDD data base.

Atomic Force Microscope (AFM) was used to observe surface topography of carbon and HAP films and to define its Ra parameter by Veeco Multimode with a NanoScoper controller.

C/HAp coatings was investigated using Hitachi S-3000N scanning electron microscope (SEM) equipped with Noran X-ray energy dispersive spectroscopy detector (EDS). Penetration beam parameters were fitted to not exceed the thickness of HAp ($\approx 1\ \mu$m). Line-scans of Ca $K_\alpha$, P $K_\alpha$, C $K_\alpha$ and O $K_\alpha$ radiation in the Hap layer deposited by sol-gel method were collected.

Adhesion of the both coatings to the substrate was determined using a Nano G-200 nanoindenter by MTS Instruments and the scratch test method. Diamond cone was loaded with normal force and moved against the surface for a distance of 0÷500nm. Adhesion evaluation was based on the friction coefficient changes registered during the measuring process. Three measurements were performed on randomly chosen samples.

## 3. Results and discussion

### Carbon coatings

X-ray diffraction results (Figure 1) prove the diffusive nature of bonding between carbon film and metal base. The spectra revealed that after applying carbon layer to a substrate the peak splitting derived from austenite takes place in the direction of growth of its lattice parameter. Microhardness measured on the crossection of the sample just below nano crystalline diamond (NCD) layer was significantly higher than microhardness of the AISI 316L: 450HV and 315HV, respectively. This indicates that carbon layer (NCD) deposited by RF PACVD method is connected with the steel substrate by diffusion bonding.

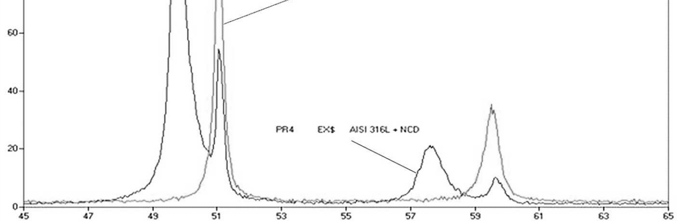

Fig. 1. Diffraction of 316L sample before and after deposition of the carbon layer

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The carbon layer of average 120 nm thick created on an AISI 316L steel base using RF PACVD method, measured by calotest method is characterized by a uniform and compact structure and average roughness of about 5 nm (Figure 2).

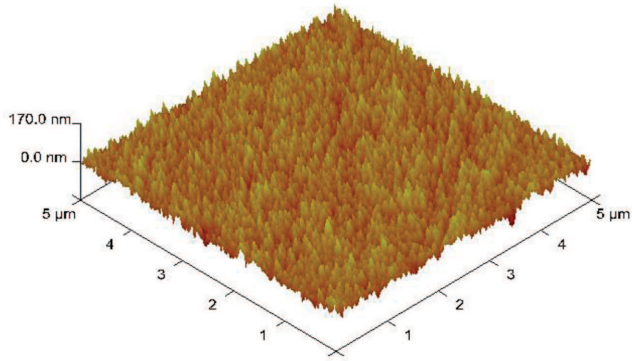

Fig. 2. AFM image of carbon layer deposited on AISI 316L substrate

The adhesion measurements of carbon layer (NCD) to the substrate are shown in Figure 3. As it shows, a significant change in the friction coefficient occurs when the force reaches a value between 70 to 100 mN.

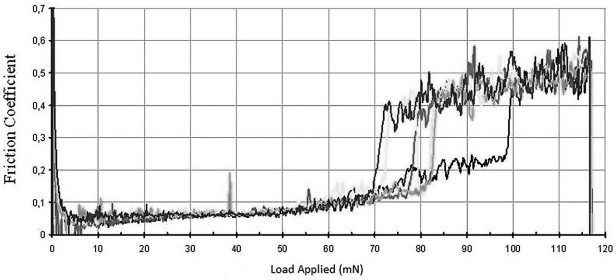

Fig. 3. Measurements of adhesion of carbon layer to AISI 316L steel base

## Carbon – hydroxyapatite composite coatings (C/HAp)

Investigations confirmed that hydroxyapatite is composed mainly of crystalline phase (Figure 4).

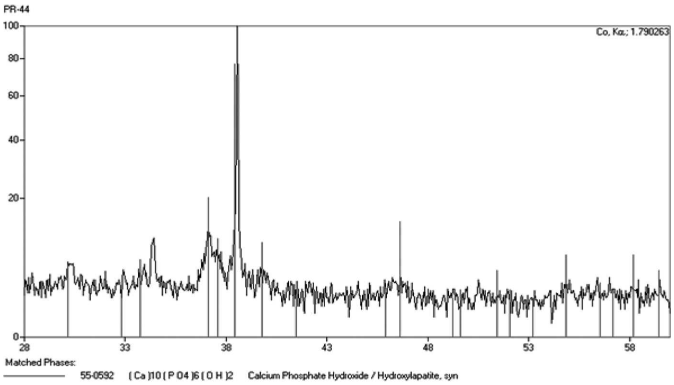

Fig. 4. XRD data of the HAp coating deposited on a Si substrate by sol-gel method

The overall thickness of the coatings was about 1 $\mu$m. Such a statement is based on EDS linescan (Figure 5) shown the increased quantity of Ca and P (the fundamental components of such layers) within this thickness.

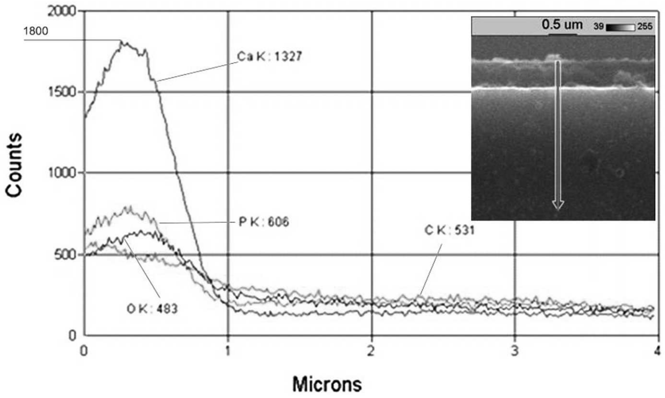

Fig. 5. Cross section and EDS line scan of the C/HAp coating deposited by sol-gel method on AISI 316L steel

Hydroxyapatite coatings on the 316L steel base are characterised by uniform structure composed of clusters several dozen nm in diameter and an average roughness $R_a = 9{,}55$ nm (Figure 6).

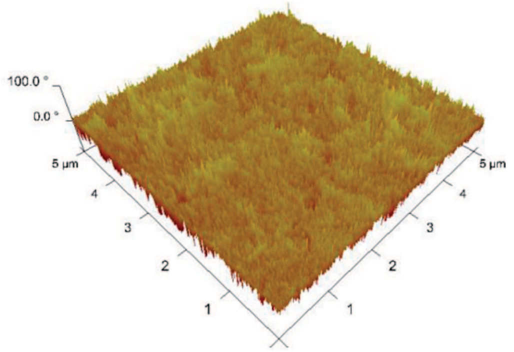

Fig. 6. AFM image of HAp coatings deposited on AISI 316L substrate

Figure (7a) shows the adhesion of HAp coating deposited on the AISI 316L steel substrate. Changes in friction coefficient can be observed from the very first nanometers of the scratch test. A dramatic change of that parameter is at the value of about 40 mN, where total delamination of HAp layer occurs. Figure (7b) illustrates the situation, where the change of friction coefficient of the composite C/HAp layer is clearly visible only between the loads of 60 and 75 mN. There is no other range on the graph where more changes in friction coefficient occurs opposite to Batory [10] where the change of friction coefficient is clearly visible at load of 70 mN. Such a behaviour can be explained by better chemical interaction between carbon and hydroxyapatite deposited by sol – gel method, contrary to Pulse Laser Deposition.

Summarizing, the presence of carbon film is responsible for better adhesion of hydroxyapatite.

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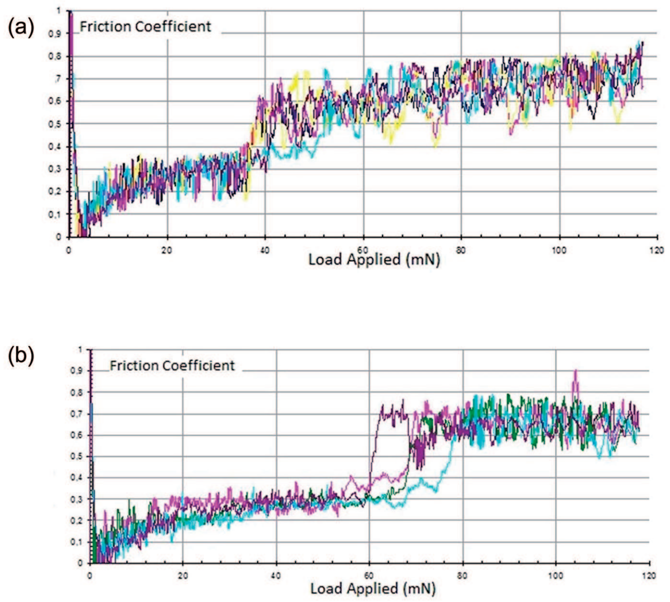

Fig. 7. Adhesion tests of HAp on AISI 316L steel substate without carbon layer (a) and with carbon layer (b); HAp was obtained using sol-gel method

## 4. Conclusions

The carbon layer of 120 nm thickness deposited on the AISI 316L steel substrate by use of RF PACVD method is characterised by a uniform and compact structure and average roughness of about 5nm. Bonding of the carbon layer and the steel substrate is diffusive in nature. The 1 $\mu$m thick hydroxyapatite coating deposited by sol-gel method has a uniform, crystalline structure and has average roughness of 9.55 nm.

Hydroxyapatite film synthesized by sol-gel method on the steel substrate with previously deposited carbon layer is characterized by its high adhesion. Taking into consideration results showinng the increase of corrosion resistance of the stainless-steel substrate with deposited carbon/hydroxyapatite layer [16], the analysed composite may be applied as long-term medical implants.

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