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Scientific paper  
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## The possibility of bioactive coatings obtaining by electrophoretic deposition of HAp on the steel implants

*Surgical metallic implants are usually made of stainless steel, titanium- and cobalt/chromium- based alloys which have superior structural and mechanical properties, and are corrosion resistant. Nevertheless, they are susceptible to local corrosion in the human body, releasing metal ions into the nearby body tissue and fluids. Keeping the advantage of their mechanical properties, their biocompatibility can be achieved through deposition the bioinert or even bioactive coating onto their surface. Hydroxyapatite is known by its bioactive behavior, originating from its chemical identity with human bones.*

*The electrophoretic deposition is rather old technique used here with a novel nanostructured hydroxyapatite powder to obtain uniform and dense hydroxyapatite coatings, to overcome the restrictions of previously used high temperature coating techniques and to overcome the complex geometry metallic substrate problems.*

*The coating of nanosized hydroxyapatite was electrophoretically deposited on blasted surface of stainless steel 316LVM samples at constant voltage, for different deposition times and subsequently sintered in argon atmosphere at 1000 °C.*

*The HAp powder thermal stability was initially assessed using DTA-TG analyses over the temperature range of 23°C-1000°C. The microstructure characterization of the coating was accomplished using SEM, and phase composition was determined by XRD.*

**Key words:** hydroxyapatite, 316LVM stainless steel, EPD, coatings

### INTRODUCTION

Hydroxyapatite is well known by its bioactive behavior, but structurally too weak to be used alone as an implant material [1, 2]. The adequate technique of hydroxyapatite coating depositing on the metallic substrate, i.e. on the implant's metal material, has been the aim of investigation for almost two decades worldwide [1-10]. Usually used metal materials for hip implants, besides the 316LVM stainless steel, are titanium- and cobalt/chromium-based alloys. Although bioinert, due to their corrosion resistance, they are not biocompatible. Besides, they are susceptible to local corrosion in the human body, releasing metal ions into the adjacent body tissue and fluids. Hydroxyapatite (HAp) is chemically identical with the mineral constituent of bones and teeth, and when deposited on the metallic implant it enables implant's biocompatibility.

Numerous technological methods of HAp coatings deposition on metallic implants were developed. Some of the most applies are: ion beam deposition, plasma spraying, sputtering, sol-gel coating and electrophoretic deposition [2-14]. The electrophoretic deposition (EPD) of HAp on metal substrates have important advantages: efficiency in obtaining dense and uniform coatings on differently shaped and thick metal substrates, high purity of formed coating, the possibility of obtaining the desired coating thickness with relatively simple process control by different parameters variation [6-9].

This process, besides EPD of a coating, consists of subsequent annealing needed for HAp powder sintering. The major problem related to the high temperature process could be the HAp decomposition. Sintering temperatures needed to achieve highly dense coatings could have caused HAp coatings phase changes, but due to the stoichiometric nanostructured hydroxyapatite powder used, the possibility to obtain a bioactive coating on 316LVM substrate, without the coatings phase changes is presented in this work.

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316LVM stainless steel is commonly used as implant material due to its mechanical properties (strength, ductility), corrosion resistance, and low cost - which can be the decisive preference [6]. Since the substrate with deposited HAp coating should be subjected to relatively high sintering temperatures, the stainless steel advantage, compared to other metal alloys, is better matching of thermal expansion coefficient with hydroxyapatite. In theory, the thermal expansion coefficient of the coating should be somewhat lower than that of the substrate [4,5]. Such thermal coefficients correlation should result in compressive residual stresses in the coating during cooling, in that way inhibiting the formation of cracks.

Sintering is unavoidable, but critical stage, because the coating must be densified after the deposition, and it occurs at temperatures of at least 1200°C for the most of commercially available HAp powders [10-14]. During the sintering stage the coating densifies, but such a high sintering temperature can cause the thermal decomposition of the coating itself, as well as the degradation of the mechanical properties of the metal implant [5]. There are studies in which authors suggested that concerning the metal implant mechanical properties, the densification temperatures should not exceed 1050°C, because up to 1050°C the tensile strength of 316LVM stainless steel was unaffected [4]. The same authors showed that HAp decomposes in the contact with metal at much lower temperatures. So, in contact with 316LVM stainless steel the typical HAp decomposition temperature of 1300°-1400°C is reduced to ~950°C [3,4]. Considering the metal substrate mechanical properties preservation, the lowering of the sintering temperature is desirable in HAp coating/metal system [8]. Minimization of the HAp densification temperature requires the use of HAp powders with maximal specific surface area, so only with as-precipitated uncalcined powders the maximal density could be reached [8]. The present work investigated the nanostructured HAp powder obtained by a novel modified spray-dry method [12]. Having in mind the proven stability of the used HAp powder [12,14], it is decided to carry out the experiments at the temperatures above those reported for a HAp decomposition, but limited with the metal substrate properties. Sintering had to be performed in argon atmosphere to prevent the interface oxidation in the presence of oxygen, which results in weak bonding of ceramic coating to the metallic substrate [5,6,9].

The possibility to obtain a bioactive coating, made of non commercial home-synthesized nanostructured HAp powder on 316LVM substrate is presented here.

## EXPERIMENTAL

The coating of nanosized hydroxyapatite was electrophoretically deposited on blasted surface of stainless steel 316LVM samples at constant voltage, for different deposition times and subsequently sintered in argon atmosphere, at 1000 °C.

The used HAp powder is synthesized by a novel modified precipitation method which is improved by spray-drying at 120±5 °C, as described elsewhere [12]. The Ca/P ratio of 1.67±0.01 was determined by ICP analyses. The powder phase composition, as well as XRD analysis of deposited and sintered HAp coatings was evaluated using X-ray diffractometer (Philips PW1710) with Cu K $\alpha$  radiation and curved graphite monochromator, measuring angle 2 $\theta$  in the range from 20° to 70°. The morphology of deposited and sintered HAp coatings was examined with a scanning electron microscope (Jeol JSM 5800). The estimation of the HAp powder thermal stability against the sintering temperature, the DTA-TG analyses were carried out using a device NETZCH STA 409EP, at heating degree of 10°C/min in the temperature range 23°-1000°C, i.e. up to the experimental sintering temperature.

The stainless steel 316LVM plates commonly used for hip implants, with dimensions of 40x15x2 mm, were used as both, cathode and anode, for electrophoretic deposition process. Metallic specimens were blasted for a better adhesion. It enabled also a clean surface; but the blasted specimens were rinsed with acetone and distilled water, dried at room temperature and stored in a desiccator before the EPD procedure.

Suspension of HAp particles was performed by agitation using magnetic stirrer of 0.5 g of the HAp powder in 100 ml of ethanol. For the suspension stability, the 10% HCl was added until pH=2.00 was reached. Both, cathode and anode were of the same dimensions at a distance of 15 mm. The deposition electrode was cathode.

The electrophoretic deposition of HAp particles on the 316LVM stainless steel substrate plates was performed at the constant voltage of 60 V. The deposition times were 30 s and 60 s. The coated specimens were drying at room temperature in desiccator before sintering. The subsequent sintering was carried out in argon atmosphere in an electric furnace, at 200 °C, previously degassed for 1 h, and heated up to 1000 °C, with heating rate of approximately 10 °C/min. The samples were held at the sintering temperature for 1 h, cooled in the furnace and taken out.

## RESULTS AND DISCUSSION

The thermal stability assessment of the used HAp powder against the sintering temperature was carried out by the DTA-TG analyses, Figure 1.

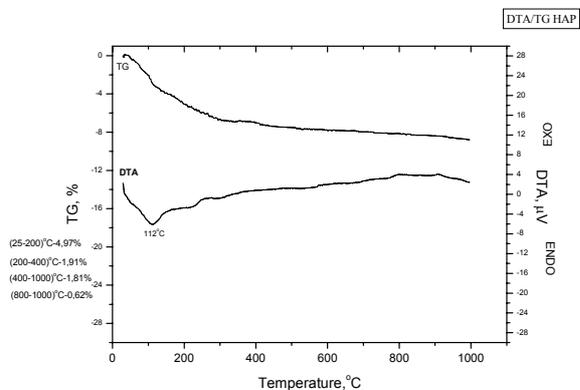


Figure 1 - DTA-TG curves of the HAp powder

The TG curve from Fig.1 demonstrates a rapid weight loss up to 200°C and a continuous slight weight loss above 200°C. Accordingly, the DTA curve shows an endothermic change at the 112°C caused by humidity release, while over the temperature range of 200°C-1000°C there was no significant DTA change accompanied to the TG change. The DTA curve has slight exothermic tendency, which does not indicate any phase change, and TG curve in the temperature range of 800°C-1000°C, has the relative change of -0.62%. This is the temperature range in which, in contact with 316LVM stainless steel, the phase transformation of HAp into the detrimental  $\beta$ -TCP (tricalcium phosphate) could have been occurred, due to HAp/metal interfacial decomposition reaction [3-5]. The typical HAp decomposition temperature of 1300°C-1400°C is reduced to ~950°C [3,4]. Here obtained results may be considered in favour of the HAp powder thermal stability over the temperature range of 23°C-1000°C, and at the experimental sintering temperature. The absence of  $\beta$ -TCP peaks at XRD pattern of the HAp coatings can also be interpreted in favour of the HAp powder stability in contact with 316LVM.

The Figure 2, presenting XRD pattern of the HAp nano-powder, exhibited peaks corresponding to the hydroxyapatite phase, indicating a low crystallinity. Figure 3 presents the XRD pattern of electrophoretically deposited HAp powder for 30 s, and subsequently heat treated for sintering in Ar atmosphere, also exhibits a very low crystallinity. The only peaks registered at Figures 2 and 3 were those corresponding to the hydroxyapatite phase. All the peaks perfectly matched the JCPDS pattern 9-432 for HAp, suggesting that the pure HAp powder was obtained

[12] and that the phase composition of the coating after EPD was unaffected after sintering processes. The compatibility of the recognized peaks at XRD patterns of the powder and of the coating leads to the conclusion that there was no phase transformation during the sintering process.

The exhibition of wide XRD peaks from the Figure 2 could be due to the low crystallinity or the result of the crystal size effect [13]. The evaluated degree of crystallinity for samples used in [13] was higher than expected from XRD pattern appearance. Accordingly, the wide peaks at XRD pattern of the HAp powder used in this investigation could be caused by very small, i.e. nanosized rod-shaped HAp powder particles, 50-100 nm in size, which were observed in previous TEM image analysis of the here used HAp powder [12]. Besides influencing the low crystallinity, this nanostructured starting powder may favour the densification process and their high thermal stability, i.e. the absence of thermal decomposition products [4,8-10,12].

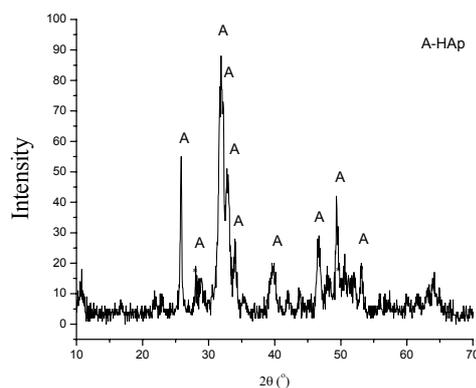


Figure 2 - XRD pattern of HAp powder

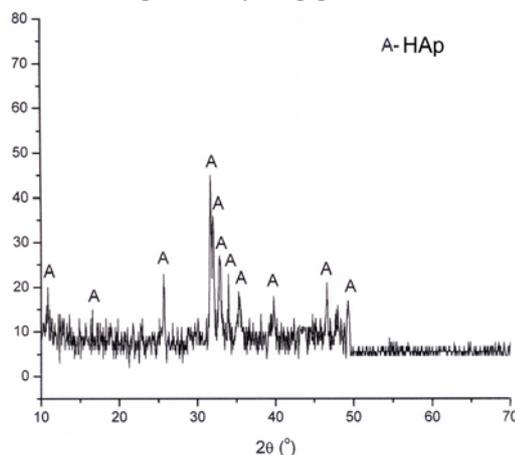


Figure 3 - XRD pattern of HAp coating

The HAp peaks were not such a wide in Figure 3, meaning that sintered powder has a better crystallinity. For samples electrophoretically deposited for 60

s and subsequently heat treated for sintering Ar atmosphere, the thicker coating was obtained, but XRD patterns were analogue to these for shorter deposition time.

The morphology has a significant impact on the electrophoretic coating quality, namely the best coatings were obtained by the rounded particles, the worst was with platy particles, while acicular particles (185nm), similar to here used powder with nanosized rod-shaped particles (sizing from 50 to 100 nm) resulted in some cracking of the coating during drying [8]. The shrinkage due to drying could be minimized by the use of regularly shape particles that can pack more efficiently. The nano-rods in the used HAp powder are almost one order of magnitude smaller than those in reported investigation, although with similar aspect ratio.

When electric field is constant, the preferential deposition of finer particles can be expected due to their higher mobility comparing to the larger particles. Knowing that the closest to the substrate the finer particles can be observed and that with shorter deposition time, only the very fine nano particles were reached the substrate surface, it can be assumed that the coating formed for shorter deposition time of 30s is made of very fine particles with low susceptibility to cracking.

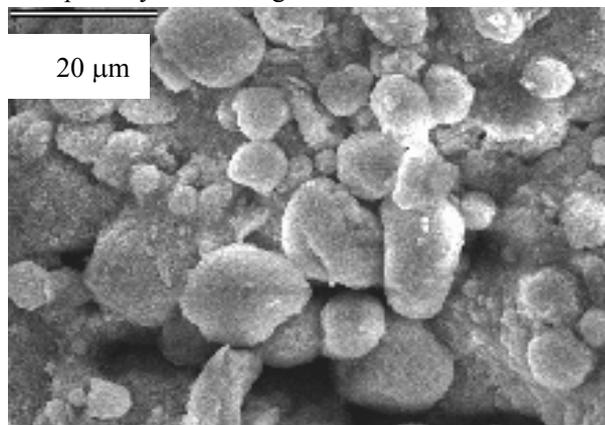


Figure 4a - Surface morphology of HAp coating obtained by EPD for 60s

The absence of  $\gamma$ -Fe peak or the peaks corresponding to detrimental structure phases, i.e. tricalcium phosphate (TCP) is evident in the presented XRD pattern of a coating sintered in Ar atmosphere at 1000°C, Figure 3. The absence of  $\gamma$ -Fe peak indicates that coating covers the substrate continuously, without pores or cracks, through which the peak originated from the substrate, could be recorded. This also means that the starting Ca/P ratio of  $1.67 \pm 0.01$  remains unchanged, favorizing the bioactivity of the coating.

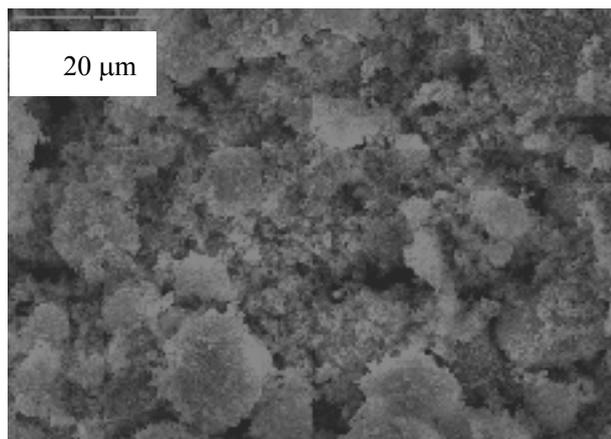


Figure 4b - Surface morphology of the 30s EPD coated and in Ar sintered sample

Figure 4a presents the morphology of a sample EPD coated for 60s, while Figure 4b presents the morphology of a sample EPD coated for 30s, and afterwards sintered in Ar atmosphere. Here, the morphology of sintered coating is visible all over the visible area. The obtained coating is comparatively uniform and free of cracks, which may be concluded by both XRD and SEM. At the XRD patterns of these Ar-sintered samples, just HAp reflections are detected. It can be concluded that the metal catalyzed decomposition of the HAp coating was not observed here, having in mind the assessed thermal stability of the powder by DTA-TG and since the XRD detected reflections belong to the original HAp.

## CONCLUSIONS

The stoichiometric Ca/P ratio of the HAp powder, along with required chemical and phase composition were important quality requirements. Here is presented a successful attempt to maintain the stoichiometric Ca/P ratio even after deposited HAp powder sintering at temperatures as high as metal substrate could resist in terms of structural and mechanical properties. The thermal stability of the used HAp powder was assessed by DTA-TG analyses and did not show any characteristic change over the temperature range of 23°C-1000°C, i.e. at the or nearby experimental sintering temperature.

The XRD patterns of the nanosized HAp powder showed the presence of characteristic HAp peaks, while the detrimental high temperature phase which could be the result of HAp decomposition was not registered. XRD patterns of the coatings sintered in Ar-atmosphere have shown just characteristic HAp peaks, meaning that comparatively continuous and crack-free HAp coatings were produced after sintering in Ar atmosphere at 1000 °C for 1 h.

The use of the stable, stoichiometric nanostructured HAp powder, synthesized by a method which produced the nanosized rod-shaped particles,

enabled obtaining the continuous HAP coatings onto the 316LVM stainless steel, where the only inherent ceramic phase is HAp.

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#### IZVOD

#### MOGUĆNOST DOBIJANJA BIOAKTIVNIH PREVLAKA ELEKTROFORETSKIM DEPONOVANJEM HIDROKSIAPATITA NA ČELIČNE IMPLANTATE

*Metalni implantati za ortopedsku hirurgiju izrađuju se najčešće od nerđajućeg čelika, legura na bazi titana, kobalta ili hroma, koje imaju odlične konstrukcione i mehaničke osobine i otporne su na koroziju. Ipak, ovakvi implantati polđožni su lokalnoj koroziji u ljudskom telu jer je zapaženo prisustvo njihovih metalnih jona u okolnim tkivima i telesnim tečnostima. Da bi se iskoristila prednost njihovih mehaničkih karakteristika, a postigla biokompatibilnost, moguće je na njihovu površinu naneti bioinertnu ili čak bioaktivnu prevlaku. Hidroksiapatit je poznat po svom bioaktivnom ponašanju, koje duguje hemijskoj istovetnosti sa ljudskim kostima.*

*Elektroforetska depozicija je relativno stara tehnika, koja je ovde primenjena uz upotrebu novog materijala – nanostrukturnog hidroksiapatita, kako bi se dobile ravnomerne i kompaktne hidroksiapatitne prevlake i tako prevazišla ograničenja prethodno korišćenih visokotemperaturnih tehnika nanošenja prevlaka i problemi sa složenim oblikom metalnog supstrata.*

*Prevlake nanostrukturnog hidroksiapatita elektroforetski su deponovane na peskiranu površinu uzoraka od nerđajućeg čelika 316LVM, pri konstantnom naponu, za različito vreme deponovanja, a zatim su sintrovane u atmosferi argona na 1000°C.*

*Toplotna stabilnost HAp praha prvo je ocenjena DTA/TG analizom u temperaturnom intervalu 23°C-1000°C. Za mikrostrukturnu karakterizaciju prevlake korišćen je SEM, a za određivanje faznog sastava XRD analiza.*

**Ključne reči:** hidroksiapatit, nerđajući čelik, EPD, prevlake

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