1. Introduction

Titanium is well known as one of the widely used metallic material for biomedical application. Commercially pure titanium (Cp-Ti) is an alternative material for AISI316L stainless steel and Co-Cr alloys due to its better biocompatibility and corrosion resistance [1,2]. However, in some biomedical applications e.g. hard tissue replacement, when high strength and good tribological properties are necessary, the Cp-Ti is unsuitable. Therefore its use in implants is restricted to applications which involve moderate mechanical stress, such as dental implants, preferentially for endosseous dental implant applications [3,4]. Such implants have direct contact with bone.

To improve the biological response to titanium, various surface engineering methods are applied. Presently, porous coatings deposited on titanium and its alloys have become an important aspect of biomaterials. Porous coatings for stabilization of implant are an alternative to bone cement fixation. Such coatings exhibit a three-dimensional interconnected array of pores, which allows bone tissue ingrowth [5]. It is very challenging to deposit a porous nanocrystalline HAp coating with controlled pore size and good adhesion to the substrate for dental implants [6]. High porosity is preferable especially for porous scaffold biomaterials [1]. However, high porosity decreased mechanical strength of porous coatings.

Bioceramics hydroxyapatite or tricalcium phosphate or bioactive glasses are known to as very important biocompatible and bioactive materials. After implantation of these bioceramics form a carbonated apatite (HCA) layer on their surfaces, which composition and structure is equivalent to the mineral phase of osseous tissue [7]. The unique properties of hydroxyapatite (excellent corrosion resistance, promoted bone cell attachment and bone formation) make them good candidates for many dental applications. Nanocrystalline HAp is more desirable than microcrystalline one because of its structural similarity with apatite [8]. Nanocrystalline particles may also contribute to better coating adhesion to the substrate.

The problems of compact porous ceramic implants are their poor mechanical properties, fracture toughness and load bearing capacity [9]. Also HAp ceramic, due to the poor mechanical properties, cannot be used for load bearing applications. The most important uses of HAp include bone graft substitutions and coatings on metallic implants. This problem is significantly reduced in the case of porous ceramic coating deposited on materials with good mechanical properties such as titanium and its alloys.

Many studies reported the importance of silica in bioactive materials for the bonding of bone [9,10]. Silica has three functions: (i) metabolic - to partake in cellular development and gene expression, (ii) chemical – as the nature of bonding to bone of bioglasses relates to the in vivo solubility of these glasses that in turn is a function of its silica content, (iii) mechanical – silica particles improve the strength of a hydroxyapatite coatings [9]. Therefore, amorphous silica particles was used in order to enhance hydroxyapatite in our coatings.

A very convenient method to deposit ceramic nano and micro particles is electrophoretic deposition (EPD) [11-13]. Electrophoretic deposition (EPD) is a two-step process. In the first step a charged particles in a stable colloidal suspension are
moved through the liquid due to electric field. In the second step
the particles are deposited on an oppositely charged conductive
substrate [12,13]. EPD enables production of a wide range of
compact or porous nano and microstructures, from nanometric
coatings up to 1 mm thick coatings. In the present work this
method was selected to deposit porous HA/SiO₂ coatings on Cp-
Titanium Grade 1. The main aim of this work was to elaborate
the EPD conditions for application of good quality coatings and
to characterize their microstructure, adhesion to the substrate
and corrosion resistance in Ringer’s solution.

2. Experimental

The samples (substrates) for the coating deposition were
made from the Cp-Ti1 material with a chemical composition
(in wt %) as follows: 0.03 C, 0.005 N, 0.001 H, 0.06 O, Ti
balance. The material was delivered by Shanghai Huaxia
Industry Co. Ltd, China. The microstructure of the Cp-Ti1
consisted of α (hexagonal close-packed) phase. The grain
diameter was in the range of 10 µm – 70 µm (Fig. 1). In some
grains an annealing twins were occurred.

![Fig. 1. Microstructure of Cp-Ti1 used as a substrate material for
casting deposition, LM](image)

The samples for coatings deposition were in the shape of
plate with the dimension of 15 mm x 35 mm and a thickness of
0.5 mm. They were ground with the use of sandpaper of 2000
grit and subsequently washed with distilled water and ethanol.

The coatings were deposited on Cp-Ti1 substrates by
EPD. A suspension for coating deposition was consisted of 1
g synthetic hydroxyapatite Ca₁₀(OH)(PO₄)₆ (HAp) containing
5 wt % SiO₂ as dopant (Sigma Aldrich, USA) and 100 ml
of ethanol. The suspension was ultrasonic treated for 40
minutes and subsequently magnetic stirred (300 rpm) at room
temperature for 10 minutes.

EPD was carried out under constant voltage conditions
in the range of 20-70 V. Deposition time was 1 minute. The counter electrode was made of austenitic stainless steel
AISI316L. The distance between electrodes in the EPD cell
was 15 mm. A heat treatment at temperature of 850 °C during
20 minutes in air was applied on coated substrates (heating rate
was 10 °C/1 min; cooling with furnace).

An influence of applied voltage and deposition time
on current density during EPD has been investigated using
Tektronix DMM 4040 multimeter. pH values were measured
using pH-meter EL20 of Mettler Toledo.

A microstructural characterization of the coated samples
was carried out using scanning electron microscopy (SEM).
The SEM investigation was performed by FEI Nova NanoSEM
450. The samples were observed directly without any surface
preparation. Chemical composition was investigated by energy
dispersive X-ray spectroscopy (EDS). The TEM investigation
was carried out using a JEOL JEM-2010 ARP microscope. A
thin foils for TEM investigation were prepared by dispersing the
powder in ethanol and stirring in order to separate agglomerated
particles. Finally, a droplet of the stable suspension was placed
on a copper grid and dried. Phase identification was performed
by selected area electron diffraction (SAED) and X-ray
diffractions (XRD). The XRD (Bragg-Brentano, B-B)
and grazing incidence X-ray diffractions (GIXRD) patterns were
recorded using a Panalytical Empyrean DY1061 diffractometer
applying Cu-Kα radiation and plan-view specimens.

Coating thickness was measured by contact profilometry.
The 5 mm trace length started in the uncoated area and finished
on the coating surface. The difference in the recorded height in
these areas was equal to coating thickness.

Coatings adhesion to the Cp-Ti1 substrate was measured by
the micro-scratch technique using a Micro-Combi Tester (MCT).
A Rockwell C spherical diamond stylus with cone apex angle
120° and tip radius 200 µm at the speed (dx/dt) of 5 mm/min was
used. Tests were done under continuously increasing load from
0 to 30 N, within the distance of 5 mm. According to the ISO
standard [14] the critical loads Lₐ₁ and Lₐ₂ that correspond to
cohesive and adhesive failures of the coating were determined.
Scratches were analyzed using acoustic emission signals and
post factum surface examination by light microscopy.

Microhardness and Young’s modulus for uncoated and
cast alloy were measured on plan-view specimens by a
MCT using instrumented indentation technique. Vickers
indenter was used and maximum load of 20 mN. At this load
penetration depth reached up to 7 µm what is about 30% of
coating thickness. The results were analyzed according Oliver
and Pharr method [15,16].

The open circuit potential and electrochemical polarization
studies of the samples were carried out using a potentiostat
Autolab PGSTAT302N. The reference was a saturated calomel
electrode and a platinum plate was used as the counter electrode.
Ringer’s solution was used as the electrolyte for the corrosion
study. The chemical composition of the Ringer’s solution
was: 8.6 g/l NaCl, 0.3 g/l KCl, 0.25 g/l CaCl₂. Measurements
were performed for pH equal 7.4 and in deaerated solutions at
temperature of 37 °C. The polarization test was performed at a
scan rate of 1 mV/s from -1.3 V to +1.5 V.

3. Results and discussion

The HAp doped Si powder, later used for coatings
deposition, was characterised by electron microscopy methods.
The SEM and TEM observation revealed the occurrence of two
types of particles: nanocrystalline with diameter up to 90 nm
and microcrystalline with size in the range of 0.1 – 1 µm (Fig. 2a,b).
The both types of particles had a spherical shape. SAED patterns analysis confirmed the presence of two phases, calcium dihydroxide hexakis (phosphate) Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ (hexagonal primitive; hp) and an amorphous phase. EDS microanalysis revealed the following mean chemical composition of the powder (in at. %): 39.3 Ca, 25.4 P, 4.6 Si and 30.7 O (Fig. 2c).

During EPD a constant voltage in the range of 20 V – 70 V was applied. Macroscopic images of as-deposited coatings are shown in Figure 3. The best quality, homogeneous coating was obtained at voltage of 60 V during 60 seconds. Thus, such parameters was selected for coatings deposition and subsequently for detailed investigation. The current density was very stable during EPD at 60 V and changed only slightly (Fig. 4a). The deposition yield might be changed by the variation of the deposition time at a constant current density. The deposits weight obtained at different deposition time during EPD with constant voltage of 60 V were investigated. The increase in the deposition time resulted in increasing of deposit weight (Fig. 4b). Nearly linear dependence between deposition time and deposit weight was found. The amount of the deposited material can be controlled by the variation of the deposition time. This founding indicates for an almost constant deposition rate. The obtained deposits were relatively dense and well adherent to the titanium substrate. Their thickness measured by contact profilometry was within 20-25 µm range. Usually coatings were thinner in their periphery.
It was found during visual inspection and SEM observation that the best quality exhibited the coatings deposited during 60 seconds (Fig. 3). Sporadically small cracks with length of 2 μm -15 μm were observed in the as deposited coatings, as illustrated in Fig. 5a. The microcrystalline HAp particles were uniformly distributed within nanoparticles formed matrix of the coating (Fig. 5b).

Thermal treatment is necessary to improve the mechanical properties of HAp. Thus, in order to densify the coatings an annealing of the coated titanium system was carried out at temperature of 850 °C for 20 minutes. It was found that annealing of as-deposited coatings led to sintering of particles and solid bridges between particles were formed. As a result of drying process, a "dried mud" cracks, characteristic for ceramic coatings, were formed. A degree of microcracking can be observed in figure 6a. The microcracking could formed during cooling and might be a result of difference in coefficients of thermal expansion (CTE) of the sintered coating and the substrate. The CTE of HAp is higher (approx. 11 x 10⁻⁶ K⁻¹ [17]) than that of the titanium substrate (8.6 x10⁻⁶ K⁻¹ [18]). However, the difference is not high and the residual stresses should be minimized. In fact, residual stresses might be introduced by oxidation of the titanium and chemical reactions during annealing at 850 °C. It is well known [19,20] that titanium has poor oxidation resistance above 300 °C and titanium oxides quickly form at elevated temperature.

The coatings exhibit high open porosity. The pore diameter distribution along the coating surface was very broad, from few nm up to 1 μm (Fig. 6b). The pores had an irregular geometry. Such porosity was expected, because it is known that particles with larger diameter will produce pores with larger diameter and large difference in particles diameter will produce broad diameter of pores. Thus, the pores size can be controlled by particles diameter. Due to presence of nanoparticles the coatings exhibit very high surface development.

It was observed during SEM and TEM investigation that three types of spherical particles occurred in the coating: HAp with diameter 200 – 600 nm as well as nanocrystalline HA and SiO₂ nanoparticles (with diameter up to 90 nm). The GIXRD investigation of the coating performed at low incidence of 1°
revealed occurrence of peaks of HAp - Ca₉(PO₄)₆(OH)₂ (hp) (Fig. 7). The presence of small peaks of SiO₂ phase was also observed in GIXRD spectrum. SEM – EDS microanalysis of chemical composition confirmed the presence of Ca, P, Si and O in the coating.

**Fig. 7.** GIXRD spectrum of the coating performed at low incidence of 1°

The SiO₂/HAp coating exhibits relatively low adhesion to the titanium substrate, typical for porous ceramic. During scratch-tests a cracks and coating delamination from the underlying substrate were observed at 5 N load. The thicker coatings have higher critical loads, what is presented in Ref. [21]. McEntire et al. [22] discussed adhesion of HAp coatings and pointed out huge effect of deposition technique. The better adhesion to metallic substrates than coatings deposited by electrophoresis exhibited these sputtered or applied using Ion Beam Assisted Deposition (IBAD). The mechanical properties and adhesion of HAp coatings can be enhanced by few treatments like deposition of interlayers between HAp and substrate, heat treatment or deposition of coatings with addition of other ceramic particles like SiO₂, TiO₂.

An average measured coating hardness was 29 ± 15 MPa. The significant scatter of the results is due to great coatings porosity what had a big effect on indentation process. These hardness values are typical for such porous coatings. Although Charitidis et. al. [23] report that hardness of HAp coatings can reach few GPa. It is confirmed by Melero et al. [24] for thick and compact HAp coatings deposited by high-velocity oxy-fuel (HVOF) spraying. They have hardness excided 3 GPa due to introduction into coatings 20% of TiO₂ particles and the low porosity equalled to 5-8%. Whereas it should be pointed the low Young’s modulus of the coatings of 1.1 ± 0.4 GPa, similar to the elasticity modulus of cancellous bone.

The influence of coating on corrosion resistance of titanium was investigated in Ringer’s solution. Figure 8 shows the evolution of the OCP for the uncoated and SiO₂/HAp coated Cp-TiI samples. It can be seen that the potential of uncoated and coated titanium was stable in time and equal -0.25 V and -0.06 V (vs SCE), respectively. The observed shift in OCP to positive values for SiO₂/HAp coated sample may indicate reduction of the driving force for the corrosion process [25]. Thus, the obtained results suggest that the SiO₂/HAp coating exhibits improved corrosion resistance in comparison to uncoated Cp-TiI.

**Fig. 8.** Evolution of open circuit potential vs. time of tested uncoated and coated Cp-TiI in Ringer’s solution at temperature of 37 °C

Figure 9 shows the anodic polarization curves for uncoated Cp-TiI and coated SiO₂/HAp samples. For the examined materials, similar courses of the obtained curves for the rate of the potential change equaling 1 mV/s was observed. The polarization curves obtained for the tested samples confirmed the results of the open circuit potential tests, which demonstrated that the SiO₂/HAp coating on Cp-TiI is characterized by a higher corrosion resistance than the uncoated one. Potentiodynamic polarization curves exhibited a passive range from the potential of the cathodic-anodic transition (-0.06 V) for Cp-TiI, - 0.28 V for SiO₂/HAp coating for the value equal about 3 V, after which an increase of the current values took place. In the case of SiO₂/HAp coating the passive range was minimally longer than in the case of the uncoated titanium. Moreover, for the SiO₂/HAp coating, both the cathode and anode currents were slightly lower than those for the uncoated Cp-TiI.

**Fig. 9.** Anodic polarization curves for Cp-TiI and SiO₂/HAp coating on Cp-TiI in Ringer’s solution at 37 °C and 1 mV/s
4. Summary

The porous composite SiO2/HAp coatings were produced on Cp-Ti Grade 1 by EPD. SEM images showed that the microstructure of the as-deposited coatings was porous, with some cracks appearing on its surface. Heat treatment of the coated specimen performed at 850 ºC leads to sintering of the particles. The coatings were 20-25 µm thick and consisted of spherical microcrystalline HAp as well as nanocrystalline HAp and SiO2 nanoparticles. Characteristic “dried mud” cracks were formed within the coatings during drying process after heat treatment.

The coating adhesion to the titanium substrate is typical as for the porous ceramic coatings. In the scratch tests cracks and coating delamination from the underlying substrate was observed at load of 5 N.

The electrochemical measurements showed the results characteristic for materials of a very high corrosion resistance. Comparison of the corrosion characteristics (open circuit potential, polarization curves) of uncoated and coated samples revealed that the overall corrosion resistance property of the SiO2/HAp coating on Cp-Ti1 was slightly better than that of the uncoated titanium.

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