

Bioactive glass–apatite composite coating for titanium implant synthesized by electrophoretic deposition

D. Stojanovic^a, B. Jokic^b, Dj. Veljovic^b, R. Petrovic^b, P.S. Uskokovic^b, Dj. Janackovic^{b,*}

^a Medical Centar Vracar, Bojanska 16, 11000 Belgrade, Serbia and Montenegro

^b Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia and Montenegro

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Abstract

Titanium and titanium alloys are widely used as materials for implants, because of their mechanical properties and nontoxic behaviour, but unfortunately, are bioinert. In order to solve this problem, the metal implant could be coated with bioactive materials with good adhesion to metal and could be also bonded interfacially to the bone.

The aim of this work is to investigate the synthesis of functionally graded glass–apatite coating on Ti6Al4V alloys by the electrophoretic method. In order to enhance bioactivity of the surface, nanostructured hydroxyapatite particles were embedded in the glass coating. The influence of synthesis condition such as deposition voltage and time on the coating properties and deposit weights were examined. It was shown that controlling the deposition voltage and time, the deposition weight and thickness of coating could be controlled. It was shown that electrophoretic deposition can be successfully employed for the preparation graded glass–apatite coating on Ti6Al4V substrate.

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1. Introduction

Titanium and titanium alloys are widely used as materials for implants, because of their mechanical properties and nontoxic behaviour. Unfortunately, metallic implants are bioinert, which could be attached to the bone through form fit or frictional connections. This can lead to encapsulation by dense fibrous tissue in the body. As a consequence, non-appropriate stress distribution at the bone–implant interface appear, which can lead to interfacial failure and loosening of the implant.

In order to solve this problem, the metal implant could be coated with bioactive materials with good adhesion to metal and which could be also bonded interfacially to the bone.^{1–3} One approach is to use hydroxyapatite (HAP) coating obtained by sputtering,⁴ plasma spray processing technique,⁵ sol–gel⁶ or aerosol–gel method,⁷ hydrothermal reaction⁸ or electrophoretic deposition.^{9–11}

Another approach is to coat the implant with bioactive glass that could provide interfacial attachment to the bone. Although glass coatings based on Bioglass® have an excellent in vitro

behaviour, the thermal stresses generated as a consequence of differences in the thermal expansion between the glass and the metal, resulted in cracks appearing at the glass–metal interface. In order to solve this problem, Tomsia and coworkers^{2,12,13} developed the glasses with composition with a similar thermal expansion to the Ti6Al4V substrate. The softening point of these glasses is lower than the temperature of $\alpha \rightarrow \beta$ transformation of titania. At the same time, glass coatings with silica contents lower than 60 wt.% has shown good in vitro behaviour in SBF,³ and other with silica content higher than 60 wt.% had a better mechanical stability and adhesion to the substrate but are no longer bioactive. Functionally graded bioactive glass coating developed by the same researchers^{14–16} provided all of mentioned requirements. Using conventional enameling technique or dip-coating method, controlling the gradient in the glass composition along the coating or incorporating HAP particles into the glass, they performed a coating with excellent adhesion to the substrate and bioactivity of the surface.

Electrophoretic deposition (EPD),^{17,18} which is a colloidal process wherein ceramic bodies or coatings are shaped directly from a stable colloid suspension by a dc electric field, seem to be very promising in developing glass or ceramics functionally graded coating with different thickness on the substrate of complex shapes. The electrophoretic deposition conditions such

* Corresponding author. Tel.: +381 11 3370489; fax: +381 11 3370387.
E-mail address: nht@tmf.bg.ac.yu (Dj. Janackovic).

as deposition voltage, current, concentration and time are very important if the thickness, morphology or composition profile is to be controlled.

The aim of this work is to investigate the possibility of developing the functionally graded bioactive coating on Ti6Al4V substrate by using electrophoretic deposition. The influence of EPD parameters such as deposition voltage and time of deposition on the coating morphology and deposit weight were examined.

2. Experimental

Synthesis of glass 6P61 in the system $\text{SiO}_2\text{--Na}_2\text{O--K}_2\text{O--CaO--MgO--P}_2\text{O}_5$ were performed according to the procedure described by Tomsia and coworkers.¹⁷ SiO_2 (99%) (Silica Gel, Redondo Beach), CaCO_3 (99%) (Kemika, Cro), MgCO_3 (99%) (Kemika, Cro), NaH_2PO_4 (99%) (Centrohem, SCG), Na_2CO_3 (Zorka, SCG), K_2CO_3 (99%) (Kemika, Cro) were used as reagents. The mixtures were fired in air at 850 °C for 1 h and further at 1500 °C for 2 h in a Pt crucible and quenched. The glass was milled during 1 h at radial velocity 396 min^{-1} in a planetary agate ball mill (Fritsch, Germany), with four cups each having the volume of 600 ml. The grinding was performed using ZrO_2 grinding balls each having 5 mm in diameter. The glass to balls ratio was 20 g:400 g. Traces of ZrO_2 particles were not observed in the X-ray diffractogram of milled glass.

Synthesis of calcium hydroxyapatite particles were performed according to method described earlier,^{19,20} by dissolving 0.55 g CaCl_2 , 0.74 g $\text{Na}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$, 0.6 g NaH_2PO_4 and 0.6 g urea (all reagents were p.a. grade, Merck) in 100 ml of distilled water. The solution was annealed at 160 °C during 3 h in a sealed tube. The particles were further washed with distilled water and dried at 105 °C during 2 h.

For an electrophoretic deposition the glass suspensions were prepared by magnetic stirring 1.5 g of glass particles in 90 ml of ethanol. In order to achieve nonagglomerated particles, the suspension is ultrasonically agitated during 10 min. Electrophoretic deposition experiments were performed at various voltages (at 30, 50 and 75 V) and times (2, 5 and 10 min). The distance between the electrodes was 15 mm. As a cathode and anode, 30 mm × 15 mm × 1.5 mm plates made of Ti6Al4V surgical alloy, previously abraded and washed in acetone and distilled water, were used. As a source of constant voltage, the dc Power Iskra MA 4103 is used.

Suspension of HAP particles was performed by agitation of 0.5 g of HAP particles in 100 ml of ethanol. In order to obtain more stable suspension, the 10% HCl was added until pH value 2.00 is reached. The electrophoretic deposition of HAP particles on Ti6Al4V substrate was performed at the voltage of 30 V, which was found to be optimum for the synthesized HAP particles. The suspensions of glass and apatite particles are not stirred during the electrophoretic depositions.

The obtained deposited substrates were dried at 105 °C for 12 h and introduced in furnace at 550 °C for 5 min, annealed at the same temperature in vacuum for 7 min and heated up to 880 °C with the heating rate at 50 °C/min. The specimen was held at this temperature for 1 min and quenched in air.

The surfaces of the coating, as well as the polished cross-sections, were examined by optical and scanning electron microscopy Jeol T-20.

3. Results and discussion

The SEM micrograph of milled glass powder is shown in Fig. 1.

It is obvious that glass particles (shown in Fig. 1), milled in planetary mill under the described conditions, have an irregular shape and particle size distribution ranging from 0.3 to 0.8 μm .

The SEM micrograph of synthesized HAP particles is shown in Fig. 2. By observing this figure, it is obvious that the synthesized HAP particles are spherical having the size in the range from 3 to 5 μm . Each particle consists of great number of agglomerated nanosized needle like subparticles.

Fig. 3 shows the dependence of electrophoretically deposited weight of glass particles on Ti6Al4V substrate on deposition voltage, at constant deposition time, which was 10 min. It is shown that increasing of applied voltage results in higher deposition yields.

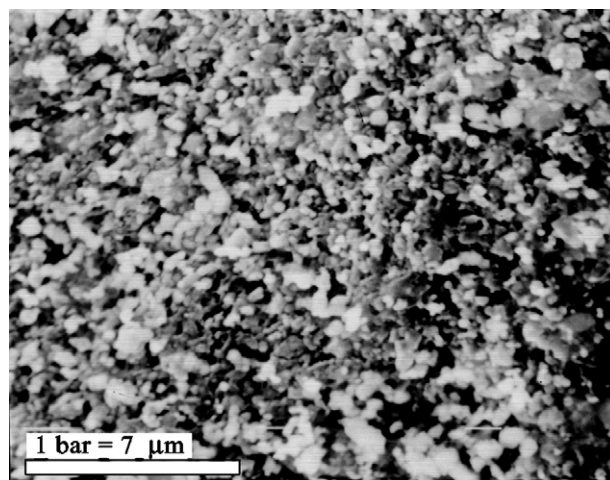


Fig. 1. SEM micrograph of milled glass particles.

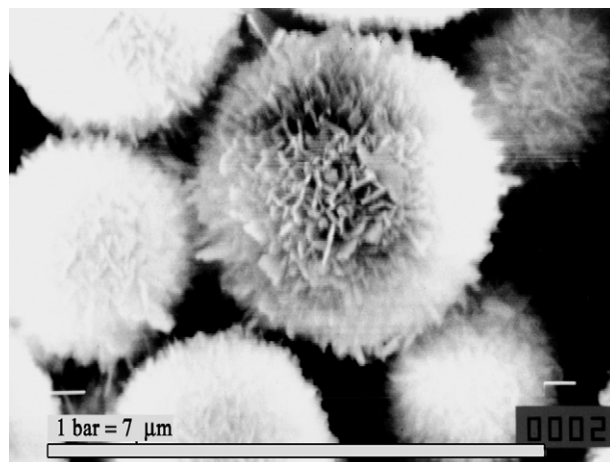


Fig. 2. SEM micrograph of HAP particles.

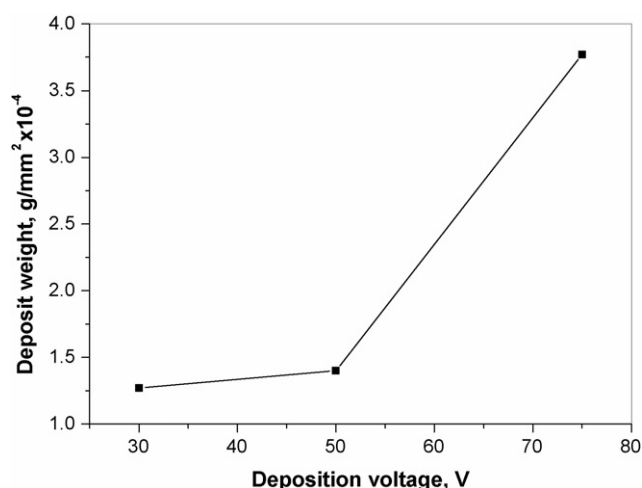


Fig. 3. Dependence of deposit weight of glass particles on deposition voltage at constant deposition time of 10 min.

The dependence of deposit weight of glass particles on deposition time at constant deposition voltage of 75 V is shown in Fig. 4. The linear dependence of the deposit weight on time up to 10 min of deposition is observed.

The Hamaker equation,²¹ which was changed over the past period, explains that the deposit weight W (kg) corresponds to the product of the electrophoretic mobility μ (m²/(V s)), the local electric field E (V/m), the electrode surface S (m²), concentration of suspension C (kg/m³) and time of deposition t (s). Assuming that μ , E , S and C are constants, the Hamaker's equation can be expressed as

$$W = \mu E S C t \quad (1)$$

The electrophoretic mobility can be described by the Smoluchowski equation:

$$\mu = \frac{\varepsilon \zeta}{4\pi\eta} \quad (2)$$

where ζ is the zeta potential, ε the dielectric constant and η is the viscosity.

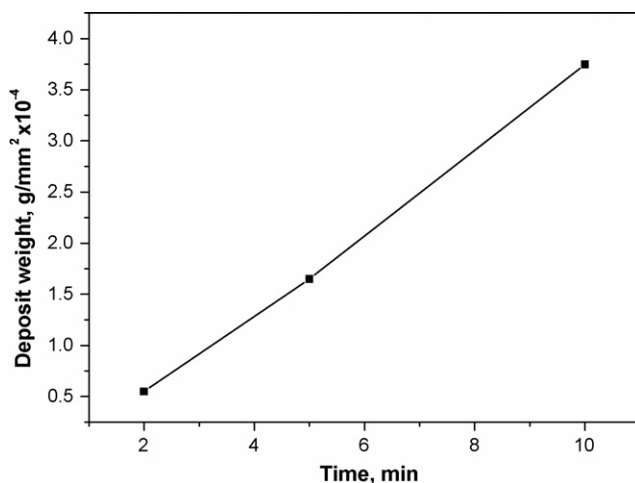


Fig. 4. Dependence of deposit weight of glass particles on deposition time at constant deposition voltage of 75 V.

In accordance with Eq. (1) deposit weight was found to increase with increase of deposition voltage and deposition time, as it is shown in Figs. 1 and 2. It was earlier found that increase of coating thickness during deposition process results in higher voltage drop in the deposit and as a consequence the decrease in deposition rate with time was observed.²² Further, electrophoretic velocity could be expressed as

$$v = \frac{\zeta E \varepsilon}{4\pi\eta} \quad (3)$$

where $E = U/d$ is potential gradient. Velocity v in Eq. (3) is a proportional to the $QE/r\eta$ where Q is charge and r is radius of particles.²² That means that particles having Q/r ratio have different electrophoretic mobilities and segregation effects can be expected in the electrophoretic deposition process. In our case, the glass particles have a radius ranging from 300 up to 800 nm. It is expected that the particle mobility, according to previous equations, is different for the particles of various radius. Further, during deposition process, the sedimentation of particles is also observed. At lower deposition voltage (30 and 50 V), the particle electric field is not to high to enable higher mobility of smaller and larger particle which sedimentate during the process. As

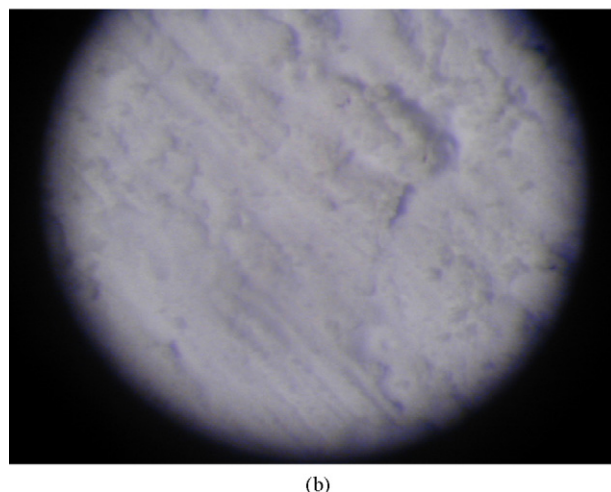
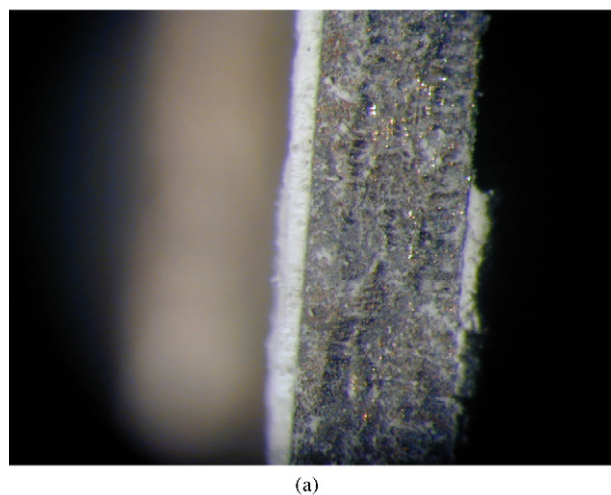


Fig. 5. Cross-section and surface view of the glass coating obtained by electrophoretic deposition, 10 min, 75 V.

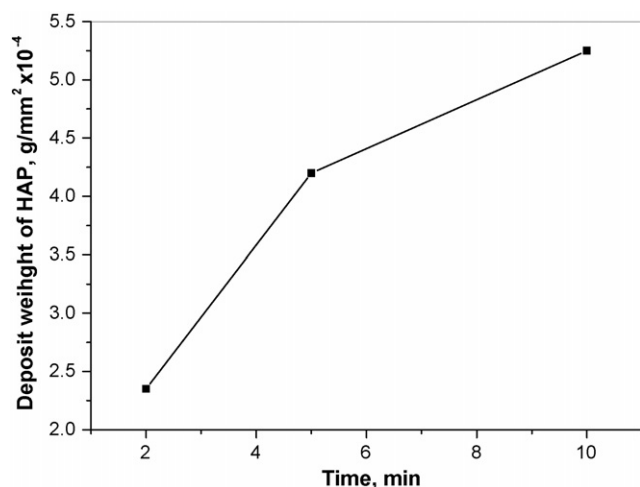


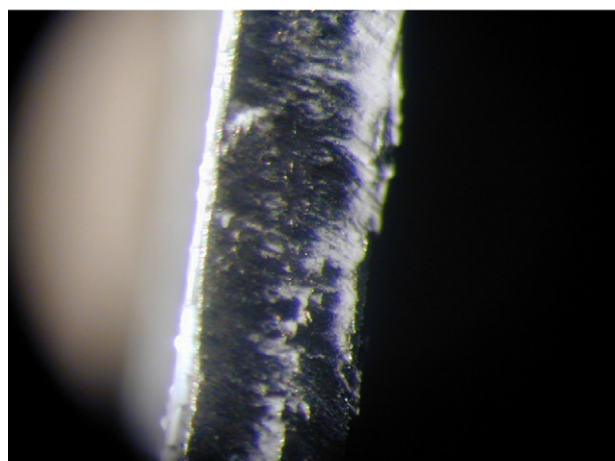
Fig. 6. Dependence of deposit weight of HAP particles on deposition time at constant deposition voltage of 30 V.

a consequence, a lower deposit weight is observed. With the increase of the deposit voltage up to 75 V, the potential gradient is high enough to enable mobility of larger particles towards substrate, and not to permit sedimentation. As a consequence of

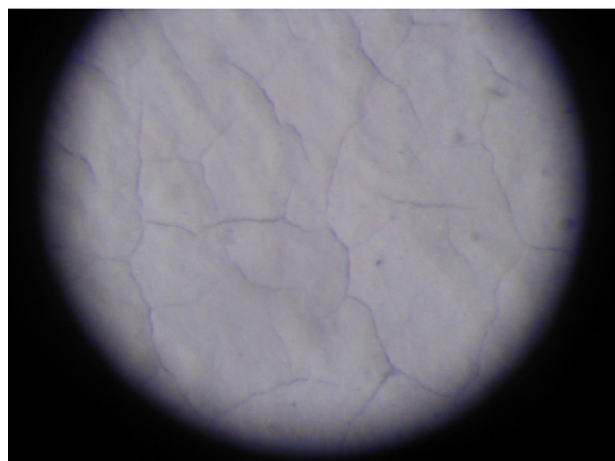
this process, the higher deposit weight is measured. In this way, the non-linear dependence and increase of the deposit weight on applied voltage, as shown in Fig. 3, could be explained. The linear dependence of deposit weight on time at 75 V, shown in Fig. 4, is expectable according to Eq. (1), due to the fact that the concentration of suspended particles has practically little changed during the deposition time of 10 min. It also seems that voltage drop, as a consequence of increasing coating thickness, is not dominant in this process.

Fig. 5 shows cross-section and surface of the glass coating, which is electrophoretically deposited on the Ti6Al4V alloy in depositing times of 10 min at the 75 V. Photos of the samples reveal dense and uniform surface of the coating without cracks and bubbles.

Fig. 6 shows deposit weight of HAP particles in dependence of deposit time. It could be observed that there is no linear dependence of deposit weight on time and that the slopes of curve decrease with time. This could be a result of the electric field decrease as a consequence of the coating thickness increase. Additionally, during electrophoretic deposition the concentration of HAP in the suspension is decreasing, which could be attributed to the deposition of particles on substrate and par-

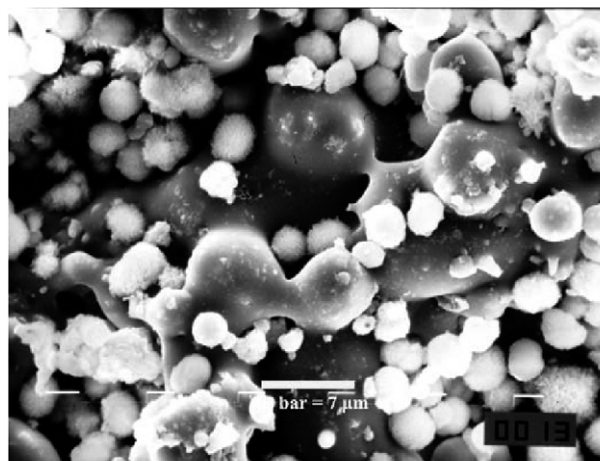


(a)

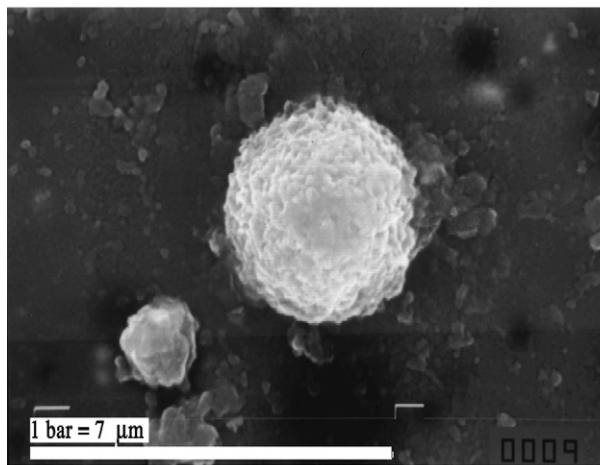


(b)

Fig. 7. Cross-section (a) and surface view (b) of the HAP coating obtained by electrophoretic deposition, 5 min, 30 V.



(a)



(b)

Fig. 8. SEM micrograph of graded glass-apatite coating on Ti6Al4V: (a) early stage and (b) final stage of heat treating.

tial sedimentation of the particles (which is observed during the deposition process).

Fig. 7 shows the cross-section and surface views of HAp coating, which is not thermally treated, electrophoretically deposited on Ti6Al4V alloy in deposit times of 5 min at 30 V. By examining photos of apatite layers, the coatings yielded during longer deposition times had higher thickness and density with less porosity. Uniform coatings were obtained with visible cracks as a consequence of drying after electrophoretic deposition.

Fig. 8 shows the heat treated grade glass–apatite coating obtained by electrophoretic deposition of glass and apatite particles. In figure (a), the early stage of heat treating is presented showing the beginning of glass melting and incorporation of apatite particles into the coating. In figure (b), the embedded HAP particles in to the coating after complete heat treatment are shown.

4. Conclusion

In this work the synthesis of functionally graded glass–apatite coating on Ti6Al4V alloys by the electrophoretic method is presented. The influence of synthesis conditions such as deposition voltage and time on the coating properties and deposit weights were examined. It was shown that by controlling the deposition voltage and time, the deposit weight and coating thickness could be controlled. The non-linear dependence of deposit weight on applied voltage could be explained by different mobility of particles with different radius, and sedimentation of larger particles during deposition process. It was shown that electrophoretic deposition is a promising method for the preparation graded glass–apatite coating on Ti6Al4V substrate.

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