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ARC PLASMA DEPOSITION OF TiO_2 NANOPARTICLES FROM COLLOIDAL SOLUTION

Vesna Maksimović[1], Milovan Stoiljković[2], Vladimir Pavkov[1], Jovan Ciganović[2], Ivana Cvijović-Alagić[1,]*

[1]Center of Excellence "CEXTREME LAB", Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia
[2]Laboratory of Physical Chemistry, Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia

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Abstract

Surface modifications of metallic biomaterials can in great merit, improve the properties of the hard-tissue implants and in that way contribute to the success of the surgical implantation process. Coating deposition stands out as one of the many surface-modifying techniques that can be used to improve implant surface properties and, in turn, induce successful osseointegration. Deposition of the TiO_2 layer on the surface of the metallic implants has a great potential to enhance not only their osseointegration ability but also their biocompatibility and corrosion resistance. In the present study, the possibility of successful deposition of the TiO_2 layer on the surface of commercially pure titanium (CP-Ti), as the most commonly used metallic implant material, by spraying the colloidal nanoparticles aqueous solution in the electric discharge plasma at atmospheric pressure was investigated. To characterize the colloidal TiO_2 nanoparticle solution, used for the coating deposition process, transmission electron microscopy (TEM) was utilized, while scanning electron microscopy (SEM) and optical profilometry were used to investigate the deposited surface layer morphology and quality. Estimation of the deposited film quality and texture was used to confirm that the arc plasma deposition technique can be successfully used as an advanced and easy-to-apply method for coating the metallic implant material surface with the bioactive TiO_2 layer which favors the osseointegration process through the improvement of the implant surface properties. The TiO_2 coating was successfully deposited using the arc plasma deposition technique and covered the entire surface of the CP-Ti substrate without any signs of coating cracking or detachment.

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[*] Corresponding author: Ivana Cvijović-Alagić, *ivanac@vinca.rs*

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Introduction

Metallic biomaterials are successfully used for decades in biomedicine for the production of hard-tissue implants designed to substitute the loss of a specific body part, organ, or function [1-3]. Biometallic implant materials are applied not only in orthopedic and dental surgery but also in cardiovascular surgery and otorhinolaryngology. Further development of biometallics and improvement of their properties must always be in accordance with the specific biomedical application requirements and imperative to produce the more durable implants which can withstand significant biomechanical loads, provide high functionality in the corrosive environment, and safe service during the interaction with living cells and tissues [3, 4]. Since implant damage can significantly deteriorate the patient's health, the research in this material science field is directed toward the obtainment of biometallic materials with improved biocompatible properties and new surface modification solutions aimed to optimize the performance of the implant in the demanding human body conditions [2, 3, 5].

Titanium-based materials are the most commonly used biometallics due to their exceptional biocompatibility and corrosion resistance, low cytotoxicity, and good mechanical properties [3, 5, 6]. However, further improvement of their properties is still one of the major challenges of the modern age material science engineering to obtain more durable implants with prolonged functionality, in the physiologically acceptable manner, following the principles of economically acceptable production. Namely, the economic aspect of high-quality implant manufacture cannot be disregarded since their economic production leads to the obtainment of more affordable medical devices attainable for a wider group of patients. Having all this in mind, the modification of already used biometallic materials stands out as an economically acceptable and efficient solution for the fabrication of durable implants with improved characteristics [7,8]. Application of suitable surface modification method allows the retainment of good mechanical properties of the implant material with simultaneous attainment of its improved surface characteristics, such as implant bioactivity, biocompatibility, osseointegration ability, and corrosion resistance, by modification of its surface chemistry and morphology. Different surface modification technics, such as chemical etching and coating, ion implantation and deposition, anodic oxidation, etc., can be used for this purpose [7]. However, arc plasma deposition can be singled out as an easy-to-apply coating deposition technique that offers the possibility to deposit different types of coatings on the surface of the metallic implants depending on their medical application requirements [7, 9, 10].

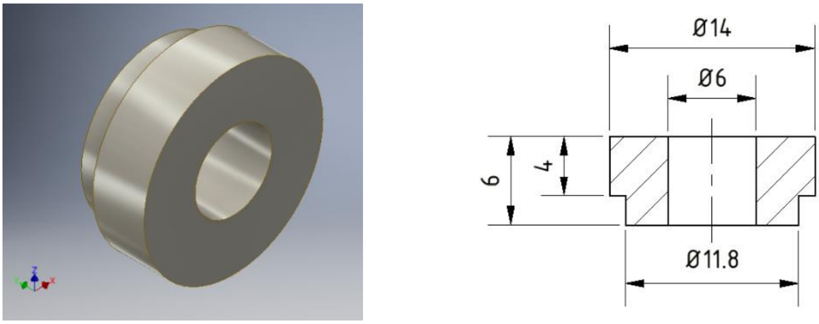
Commercially pure titanium (CP-Ti) is a widely used implant material, and modification of its surface properties is considered a simple, effective and economically acceptable solution for the obtainment of damage-resistant implants with enhanced bioactive characteristics. Bio-functionalization of the CP-Ti surface by deposition of bioactive surface coatings shows significant potential for the obtainment of the enhanced implant osseointegration properties [11]. Namely, bone ingrowth into a metallic implant can be favored by deposition of the diverse surface layers characterized by the specific morphological features which will favor live cells adhesion and proliferation [12-14].

Recent studies showed that the TiO_2 coating deposition influences the enhancement of antimicrobial, biocompatible, and corrosion-resistant properties of the substrate [15-17].

Therefore, the aim of the present study was to investigate the possibility of the successful deposition of continuous TiO_2 coating on the CP-Ti surface by easy-to-apply arc plasma deposition method and in that way obtain topography and texture of the implant material surface favorable for the bone ingrowth.

Experimental work

The CP-Ti grade 2 supplied by Goodfellow, Germany, in the shape of a 14-mm-diameter bar was used in this study as a substrate material for the bioactive coating layer deposition. The ring-shaped work-piece, with dimensions presented in Fig. 1, was cut from the CP-Ti bar and subjected to the standard metallographic preparation procedure and cleaning in the ultrasonic bath with ethanol to obtain an uncontaminated surface prepared for the coating deposition.



(a) *(b)*

Fig. 1. The CP-Ti substrate work-piece :(a) 3D overview and (b) schematic representation of the work-piece dimensions.

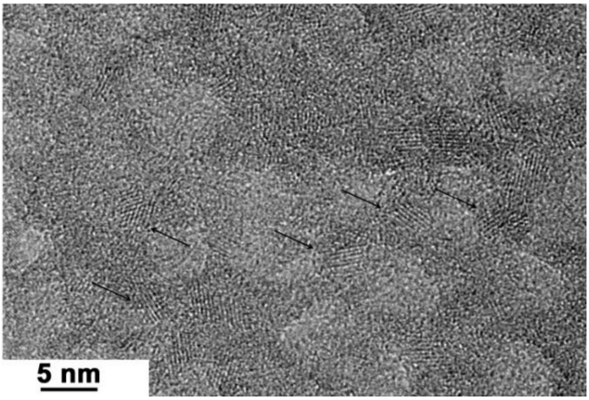
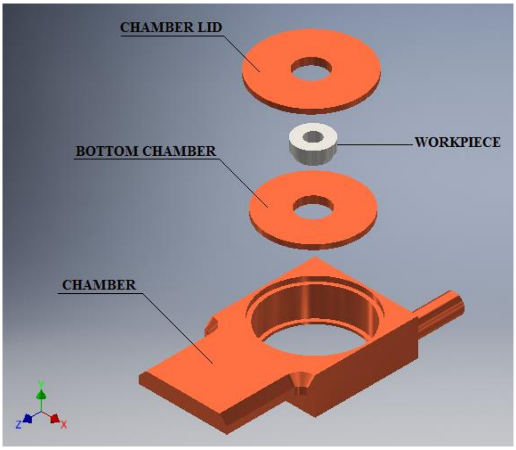


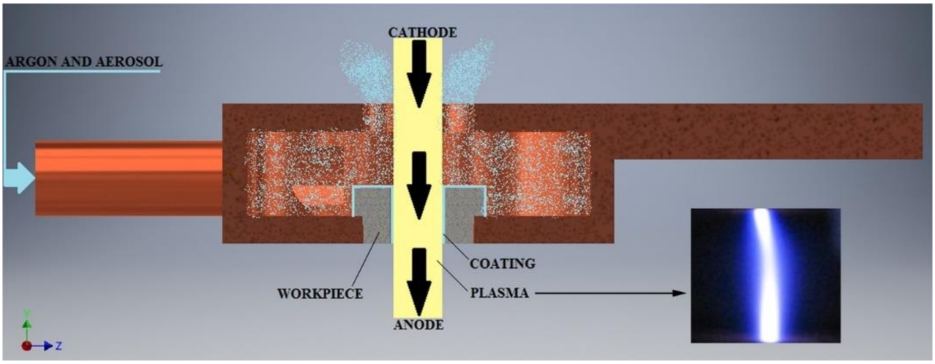
Fig. 2. TEM image of the TiO_2 colloidal nanoparticles used for the coating deposition process.

As a source for the TiO_2 coating layer deposition, the colloidal TiO_2 nanoparticles aqueous solution was used. The TEM analysis revealed that the used colloidal solution contains TiO_2 nanoparticles with a diameter ranging from 4.5 to 5 nm (see Fig. 2). Spraying of the colloidal solution with the concentration of 0.24 M, approximate particle number of 1×10^{17} particles/ml, and agglomeration number (number of TiO_2 molecules in one particle) of 1402 was conducted using the Meinhard Type A pneumatic nebulizer coupled with the Scott-type cloud chamber presented in Fig. 3. The flow of supporting argon gas was maintained at 2 dm^3/min while the aerosol yield was approximately 0.03 ml of liquid per 1dm^3 of argon. The nebulizer system generated aerosol droplets ~ 10 μm in size, while the spraying time was limited to 1 min.

The illustration of the experimental set-up used in the present investigation for the generation of the atmospheric pressure direct current (DC) arc argon plasma equipped with the aerosol sample supply is given in Fig. 3a, while the illustration of the arc plasma deposition process can be observed in Fig. 3b. Detail description of the experimental set-up was reported previously [18, 19], while its brief overview is presented in this study.



(a)



(b)

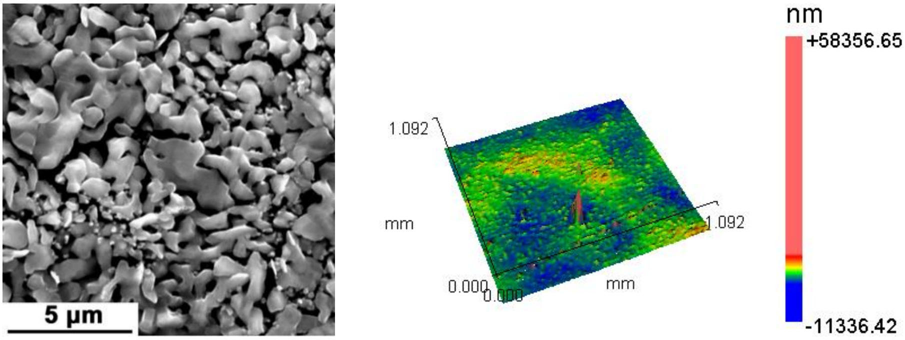
Fig. 3. Illustration of the applied arc plasma deposition (a) set-up and (b) process.

Namely, the set-up consists of plate brass segments and plate copper diaphragms that are electrically insulated and water-cooled. The current-carrying channel, *i.e.* arc plasma, is established between the copper anode rod and the graphite cathode tube, mutually coaxially oriented. The atmospheric pressure plasma was generated by DC arc discharge. The applied current was 10 A and it resulted in the formation of the arc plasma column with a diameter of approximately 4 mm. The arc plasma passes through the circular openings of the consecutive segments and diaphragms to be constricted and spatially stabilized. The mid part of the arc column goes through a chamber, *i.e.* cylindrical cavity, of the central brass. The cavity has lower and upper circular openings to avoid excessive constriction of the plasma column and to enable aerosol contact with the plasma. Aerosol, formed by the pneumatic nebulizer and carried by the argon stream, is tangentially introduced into the cylindrical cavity forming a vortex around the high-temperature plasma column. The temperature generated in the vortex center was approximately 10000 K, while at the vortex periphery, this temperature drops close to 5000 K due to the presence of a strong temperature gradient. A ring-shaped CP-Ti work-piece was fixed coaxially within the cavity of the central segment. In this way, it is enabled for the plasma column to pass through the ring-shaped work-piece and heat it. The aerosol evaporates and desolvates during its contact with the generated plasma, and as a result, the TiO_2 solids, which are partially melted, evaporated and subsequently atomized, are formed and their deposition on the CP-Ti work-piece surface is enabled.

Results and discussion

Application of the arc argon plasma deposition method at the atmospheric pressure resulted in the formation of the TiO_2 layer on the CP-Ti surface (Figs. 4-6). The SEM analysis of the deposited layer revealed that this layer is continuous and that it covers the entire surface of the CP-Ti work-piece. The presence of a strong temperature gradient in the vortex formed around the high-temperature plasma column resulted in the formation of the TiO_2 layer on the CP-Ti substrate surface with different morphological features depending on the distance from the plasma column.

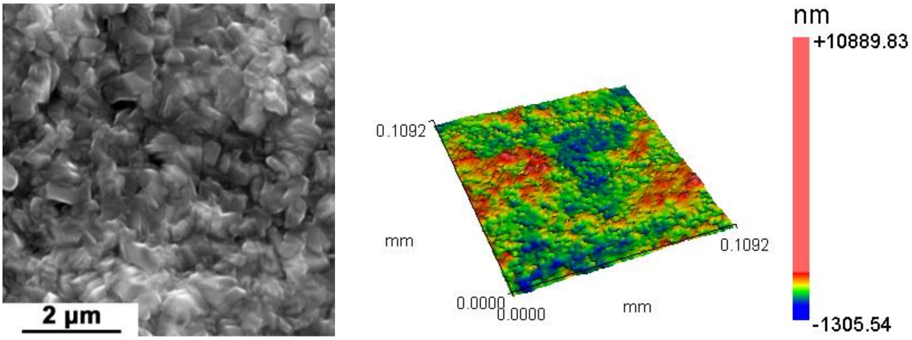
Namely, the highest temperatures generated at the positions closest to the plasma column led to the formation of the surface layer composed of the partially melted and solidified irregularly-shaped TiO_2 particles (Fig. 4a). This kind of a surface layer was formed close to the inner edge of the ring-shaped CP-Ti work-piece which is closest to the formed plasma column. The profilometric analysis of the layer deposited at the positions near the inner edge of the ring-shaped CP-Ti work-piece indicated that the average size of the deposited TiO_2 particles is 1.061 μm, while the roughness of the deposited layer positioned near the plasma column is estimated as 0.898 μm (Fig. 4b).



(a) (b)

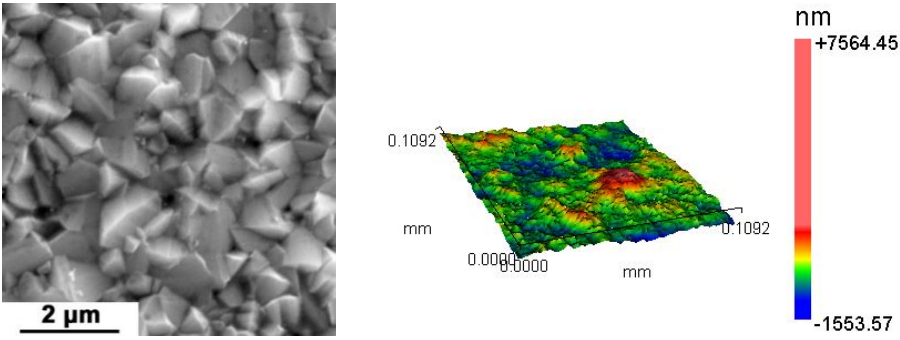
Fig. 4. The TiO_2 surface layer deposited close to the CP-Ti work-pieces inner edge: (a) SEM micrograph and (b) 3D profilometric analysis.

However, as the position of the deposited TiO_2 particles changes across the work-piece diameter their size and morphological features also change (Figs. 5 and 6).



(a) (b)

Fig. 5. The TiO_2 surface layer deposited in the central zone located between the outer and inner edge of the CP-Ti work-piece: (a) SEM micrograph and (b) 3D profilometric analysis.



(a) (b)

Fig. 6. The TiO_2 surface layer deposited close to the outer edge of the CP-Ti work-piece: (a) SEM micrograph and (b) 3D profilometric analysis.

Results of the SEM and profilometric analysis, presented in Fig. 5, indicated that in the central zone, located between the outer and inner edge of the ring-shaped CP-Ti work-piece, finer TiO_2 particles can be distinguished than in the case of the particles present at the inner edge of the work-piece. The average size of the deposited TiO_2 particles in this central zone is 0.344 μm, and this part of the surface layer is characterized with significantly lower roughness compared with the layer at the inner edge of the CP-Ti work-piece, since the estimated roughness in this area is 0.278 μm. Still, some agglomeration of the deposited TiO_2 particles was observed. Close to the outer edge of the CP-Ti work-piece, however, slightly coarser and regularly-shaped TiO_2 particles can be distinguished at the CP-Ti surface (Fig. 6). The average TiO_2 particle size at the positions close to the outer CP-Ti edge is 0.366 μm, while the roughness of the deposited coating at this position is determined as 0.304 μm. The TiO_2 particles observed close to the outer work-piece edge are quite uniform in size, pyramidal in shape and with distinct facets present, which is contrary to the TiO_2 particles deposited close to the work-piece inner edge.

Nevertheless, it must be emphasized that the deposited surface coating is continuous and that signs of coating cracking or detachment from the CP-Ti surface were not detected across the entire substrate surface. This indicates that the proposed arc plasma deposition method can be successfully used for the surface modification of the biometallic surfaces.

Conclusion

Conducted investigations confirmed that by applying the arc plasma deposition method at atmospheric pressure, a successful deposition of the stable bioactive TiO_2 layer on the CP-Ti surface can be achieved. The application of this simple and cost-effective coating deposition technique enabled a good dispersion of the TiO_2 nanoparticles onto the CP-Ti surface influencing in that way the formation of the continuous surface layer favorable for the biometallics corrosion resistance, biocompatible and osseointegration properties after their implantation into the human body. Having all this in mind, the results of the present study should be perceived as the starting point for future investigations aiming to determine the influence of the deposited TiO_2 surface layer morphology on the corrosion resistance and biocompatibility of the biometallic materials.

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