UDK 621.791.763:669.017.3
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 55(2)231(2021)

CHARACTERISATION OF BIOMEDICAL TITANIUM LAYERS DEPOSITED BY A VACUUM PLASMA SPRAY PROCESS

KARAKTERIZACIJA BIOMEDICINSKIH TITANOVIH PLASTI, NANEŠENIH S POSTOPKOM VAKUUMSKEGA PLAZEMSKEGA NAPRŠEVANJA

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Prejem rokopisa – received: 2020-07-15; sprejem za objavo – accepted for publication: 2020-12-29

doi:10.17222/mit.2020.135

In this paper we will describe the process of the deposition of thick layers of VPS-Ti coating, which is used as a bonding layer for the upper porous Ti coatings on implant substrates. In order to deposit the powder, we used HÖGANÄS Ti powder labelled as AMPERIT 154.086 -63 µm. In order to test the mechanical properties and microstructure of the VPS-Ti coating, the powder was deposited on Č.4171 (X15Cr13 EN10027) steel substrates. Mechanical tests of the microhardness of the coating were performed by the Vickers hardness test method ($HV_{0.3}$) and tensile strength by measuring the force per unit area (MPa). The microhardness of the coating is 159 $HV_{0.3}$, which is consistent with the microstructure. The coating was found to have a good bond strength of 68 MPa. The morphology of the powder particles was examined on a scanning electron microscope. The microstructure of the coating, both when deposited and etched, was examined with an optical microscope and a scanning electron microscope. By etching the coating layers, it was found that the structure is homogeneous and that it consists of a mixture of low-temperature and high-temperature titanium phases (α-Ti + β-Ti). Our tests have shown that the deposited layers of Ti coating can be used as a bonding layer for porous Ti coatings in the production of implants.

Keywords: vacuum plasma spray process, titanium, microstructure, microhardness, bond tensile strength

V članku avtorji opisujejo proces nanašanja debelih titanovih plasti s postopkom vakuumskega plazemskega naprševanja (VPS-Ti), ki se uporabljajo kot prevleke oziroma vezivni sloji zgornjih poroznih Ti prevlek na podlagah implantatov. Kot prašek za depozicijo so uporabili Höganäsov Ti prah, imenovan AMPERIT z velikostjo delcev med 154,086 µm in 63 µm. Zato, da bi določili mehanske lastnosti in mikrostrukturo VPS-Ti prevlek, so izbrani prašek nanesli na podlago iz jekla Č 4171 (X15Cr13 EN10027). Mikrotrdoto prevleke so določili z Vickersovim merilnikom trdote ($HV_{0,3}$). Natezno trdnost prevleke pa so določili z merjenjem sile na enoto preseka (MPa). Mikrotrdota prevleke je bila 159 $HV_{0,3}$, kar se ujema z mikrostrukturo. Prevleka je imela dobro vezavno trdnost – 68 MPa. Morfologijo prašnih delcev so opazovali z vrstičnim elektronskim mikroskopom, medtem ko so mikrostrukturo nanešene in jedkane prevleke opazovali tako z optičnim kot tudi z vrstičnim elektronskim mikroskopom. Jedkana mikrostruktura prevleke je bila homogena in sestavljena iz mešanice nizko- ter visokotemperaturnih titanovih faz (α-Ti + β-Ti). Izvedene preiskave so pokazale, da se lahko Ti prevleke, napršene z vakuumskim plazemskim naprševanjem, uporabi kot Ti prevleke v proizvodnji implantatov.

Ključne besede: vakuumsko plazemsko naprševanjo, titan, mikrostruktura, mikrotrdota, vezna natezna trdnost

1 INTRODUCTION

Titanium, titanium alloys and TiO_2 are the materials widely used in the implant manufacturing process.[1–3] The advantages of titanium over other metallic materials are its lower density, good mechanical properties related to its specific strength, elastic modulus and fatigue resistance. In addition to good mechanical properties, titanium is also characterised by good chemical properties and biocompatibility.[4–6] The resistance of titanium to corrosion results from its instability in air, due to which a thin and stable film of TiO_2 is quickly formed on the surface. All of the above-mentioned resulted in the further development of titanium alloys, which are widely used in orthopaedics and dentistry. Today, titanium and titanium alloys are used as primary and ideal materials for the production of artificial joints, due to their high strength and specific weight, which is close to the specific weight of human bone and exceptional resistance to the corrosion caused by the surrounding live tissue. Many years of practice have shown that titanium has good affinity for human connective tissue and bone epithelial tissue, which is very important for the biological fixation of implants.[7,8] These characteristics were especially visible in porous titanium coatings. Porous titanium coatings, deposited by vacuum plasma spray (VPS) process on titanium alloy implant substrates, provide biological activity to prostheses.[3] The porosity of the implant surface causes the growth of bone cells, which contributes to faster healing of the tissue surrounding the implant.[8] Practice has also shown that these implants, due to fatigue, abrasion wear and impact loads, maintain stable functionality with a fairly long service life.

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The VPS is most often used for the deposition of coatings on the implant elements. Depending on the type of material and its purpose, the vacuum plasma spray process enables the deposition of layers of designed characteristics in terms of their adhesive strength, density and microstructure of the coatings. Titanium, tantalum and niobium powder particles are exclusively deposited within the atmosphere of low-pressure, high-purity inert gases because these particles have a high affinity for oxygen and nitrogen.[9,10] Powders with a lower granulation are used to make binding strains from pure titanium due to the higher packing density of molten particles in the coating deposition process. Melting of titanium (Ti) powder particles within plasma as well as the cooling of folded lamellae on the substrate takes place at high speed, which causes a shift in the transformation of the high-temperature β–Ti (bcc – body-centered cubic structure) phase at temperatures below the equilibrium temperature of 882 °C.[11,12] Due to the specific melting conditions, high crystallisation rates of molten powder particles and high cooling rates of deposited lamellae, both crystalline phases of titanium α-Ti (hcp – hexagonal-close packed structure) + β-Ti (bcc) are present in the structure of the deposited coating layers.[11,12]

The main goal of this paper is to deposit thick layers of Ti coating, which, with its mechanical and structural characteristics, can be used as a bonding layer for the upper porous Ti coatings on implant substrates. In order to produce a good quality Ti coating, the powder was deposited by the vacuum plasma spray process using a low-pressure, high-purity inert gas, i.e., 99.9999 % Ar. During the deposition, we managed to avoid the influence of nitrogen and oxygen on the molten Ti particles, which was confirmed by the mechanical and metallographic testing of the coating layers. In this paper, we will present the analysis of microhardness, the bond strength between the base material and the coating and the microstructure using optical and scanning electron microscopy. Our tests have shown that the Ti coating produced at low pressure inert gas has the microstructure, microhardness and bond strength, which fully enable the application of Ti coating in biomedicine.

2 MATERIALS AND METHODS

2.1. Materials and test methods

HÖGANÄS AMPERIT 154.086 high-purity powder, in accordance with the ASTM F-1580 standard with a powder granulation of 63 µm (90 %) and 10 % a powder granulation bigger of 63 µm, was used for the deposition of Ti coating layers.[1] Scanning electron microscopy (SEM) was used to examine the morphology of the powder particles. **Figure 1** shows a scanning electron micrograph of the morphology of the applied Ti powder particles. The micrograph shows an irregular shape of the powder particles with rounded edges.

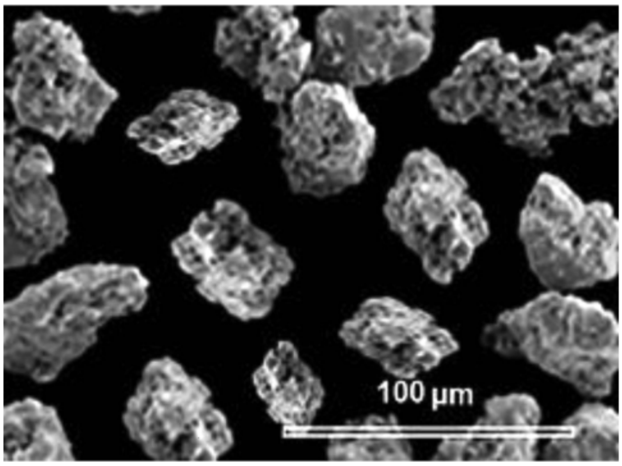

Figure 1: SEM of Ti powder particles

The substrates on which layers of Ti coating were deposited for microhardness testing and microstructure assessment were made of Č.4171 (X15Cr13 EN10027) steel in the thermally untreated condition with the following dimensions: (70×20×1.5) mm. Samples for testing the tensile strength of a (Ø25×50) mm bond surface were made of the same material. Tests of mechanical and microstructural characteristics of Ti coatings were performed according to the Pratt & Whitney standard.[13,14]

Evaluation of the mechanical properties of Ti layers was performed by testing the microhardness using the Vickers hardness test method with a diamond pyramid hardness tester load of 300 g ($HV_{0.3}$). The microhardness test was performed along the cross-section, at three measuring points, in the middle and at the ends of the sample. Five readings of microhardness values were collected and this paper presents the mean value of the microhardness for the mentioned measuring points.

Tubes composed of two paired (Ø25×50) mm specimens were used to test the tensile strength of the bond. One specimen contained deposited coating and the other was roughened with corundum (Al_2O_3) for better bonding in the gluing process. The specimens were glued, mounted and pressed against each other in a specially designed tool for specimen gluing. The specimens were glued in an oven at 180 °C for 2 h. Five glued specimens were used for the testing. Testing of the tensile strength (adhesion) of the deposited coatings was performed by the tensile method with a speed of 1 mm/min at room temperature. Coating bond strength $\sigma = F_{max}/A$ (MPa) is calculated by dividing the maximum load (F_{max}), on which the fracture occurs, by the fracture surface (A), which is calculated according to the formula $A = 3.14 \times R^2/4$, where R is the measured fracture diameter.[14] The paper presents the mean value of the bond's tensile strength.

The microstructure of the deposited coating layers, both etched and not etched, was examined on an optical and scanning electron microscope (OM, SEM). In order to see the microstructure of the deposited layers and the phases within the coating, the Ti coating was etched with a reagent of 100 mL H_2O, 2 mL HF and 5 mL HNO_3. Analysis of the pore number within the coating was performed by processing 5 photographs (OM) at a magnification of 200×. Pores were marked and shaded over a tracing paper, the total area of which was calculated based on the total area of the photographs. The percentage of pore content in the coating was measured with a software analysis of the OM photographs. The paper presents the mean value of pore number.

2.2 Plasma spray deposition

Ti powder was deposited in low-pressure inert argon gas inside the VPS system of Plasma Technik-AG with a F4 plasma gun. First, the air was pumped out in the vacuum chamber, then the pressure was decreased to 1×10^{-3} mbar for 5 min and then the chamber was flushed. The vacuum chamber was flushed two times to ensure a high degree of chamber cleanliness and to eliminate the reactivity of titanium droplets and deposited layers with oxygen and nitrogen from the surrounding atmosphere. High-purity argon gas Ar 6.0 (99.9999 %) was used to clean the chamber. For the same reason (H_2) which was used for transferred arc cleaning of the substrate and (He) which was used as plasma gas had a high degree of purity of 6.0 (99.9999 %). Before inserting the samples into the vacuum chamber and the powder deposition process, the sample substrates were roughened with white corundum particles ranging in size from 0.7 mm to 1.5 mm. A program for depositing Ti powder was made on the ASEA robot microprocessor unit and the A-2000 control panel. The program sets and synchronises all the process parameters such as: chamber vacuuming, plasma gas flow, cleaning of the substrate with transferred arc, powder flow, coating deposition, cooling of the substrate with deposited coating and vacuum chamber ventilation. The surface of the substrate was cleaned with a mixture of plasma gases Ar-$H_2^{(1)}$ and the deposition of the powder was made with a mixture of plasma gases Ar-$He^{(2)}$. The VPS parameters of Ti powder deposition on the samples are shown in **Table 1**.

Table 1: Plasma spray parameters for VPS-Ti coating

Deposition parameters	Values	
Plasma current, *I* (A)	500	750
Plasma Voltage, *U* (V)	65	74
Primary plasma gas flow rate, Ar (l/min)	50	50
Secondary plasma gas flow rate, $H_2^{(1)}$, $He^{(2)}$, L/min	$10^{(1)}$	$12^{(2)}$
Carrier gas flow rate, L/min	–	3
Powder feed rate, g/min	–	35
Stand-off distance, mm	280	290
Chamber pressure, mbar	40	130
Nozzle diameter, mm	8	8
Speed of the gun, mm/s	15	10

3 RESULTS AND DISCUSSION

In the edge zones, the coating layers had mean microhardness values of 163 $HV_{0.3}$ and 160 $HV_{0.3}$, while in the middle, the coating layers had a mean microhardness value of 154 $HV_{0.3}$. Along the cross-section, the Ti coating had a mean microhardness value of 159 $HV_{0.3}$. The low value of microhardness in the Ti coating layers is an indication that the low pressure of the high-purity argon in the vacuum chamber prevents the formation of oxides that increase the microhardness of the coating, which was confirmed by the microstructure analysis based on an optical microscope (OM). The tensile strength of the bond between the substrate and the Ti coating was 68 MPa. Roughening of the substrate and cleaning of the surface of the substrate with the transferred arc provided better adhesion of the deposited layers of the coating to the substrate, which resulted in the high value of the bond's adhesive strength. Since the sizes and number of pores, oxides and unmolten powder particles are directly related to the values of the tensile strength of the coating bond, the measured values of the Ti coating adhesive strength indicate that their presence in the coating layers is eliminated by the low pressure of the inert atmosphere found the in vacuum chamber and high purity of the applied plasma gases, which was confirmed by the microstructure of the coating layers. The values of microhardness and tensile strength of the bond were correlated with their microstructures.

Figure 2 shows the OM microstructure of the VPS-Ti coating layers in the deposited state. Qualitative analysis showed that, at the interface between the substrate and the deposited coatings, there were no defects such as discontinuities of the deposited layers on the substrates, microcracks, macrofractures and separation of the coatings from the surface of the metal substrate.

The boundaries at the interface between the substrate and the coating layers are extremely clean, which indicates good cleaning of the substrate surface with the transferred arc. No inter-lamellar boundaries are observed through the coating layers due to the good cohesion bond of the lamellae and the negligible proportion of pores. The deposited layers are quite dense and homogeneous with an extremely small proportion of pores,

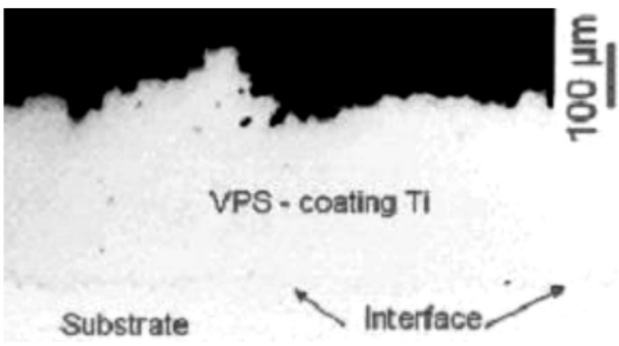

Figure 2: OM microstructure of the deposited VPS-Ti coatings

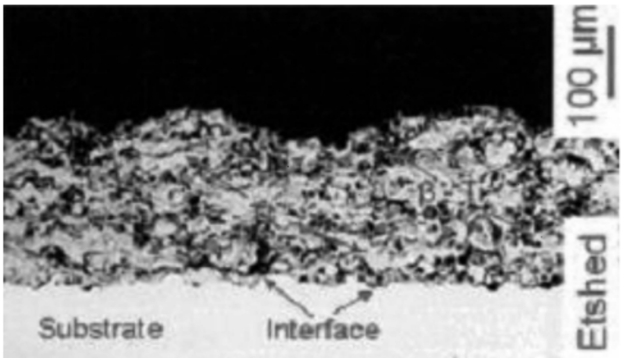

Figure 3: OM microstructure of the etched VPS-Ti coatings

which is below 1 %. The layers contained no unfused particles. No micro-cracks can be seen through the deposited layers.

In order to see the inter-lamellar boundaries and the microstructure of the deposited layers in the coating, **Figures 3** and **4** show OM micrographs showing the microstructures of the vacuum plasma spray layers of the Ti coating after they had been etched.

The microstructure of the etched VPS-Ti coating clearly shows that the inert argon atmosphere in the vacuum chamber and high purity of plasma gases at low pressure completely suppressed the oxidation of molten powder particles, which is a great advantage over the coatings deposited at atmospheric pressure. Since Ti crystallises into two crystalline forms, α–Ti (hcp) and β–Ti (bcc), it is to be expected that both phases are present in the microstructure of the deposited coating, which is confirmed by the etching of the coatings. In the microstructure of the Ti coating, two phases are clearly visible as light-grey and dark-grey fields. By etching the VPS-Ti coating, β–Ti phase (bcc) dissolves, while the undissolved α-Ti phase (hcp) stands raised as light-grey relief. As the light falls obliquely on the surface of the sample and casts a shadow over the raised α-Ti (hcp) phases, the etched β-Ti (bcc) phase colour varies from dark grey to black. The layers of the coating are evenly deposited and the microstructure of the coating is quite

Figure 4: OM microstructure of the etched VPS-Ti coatings

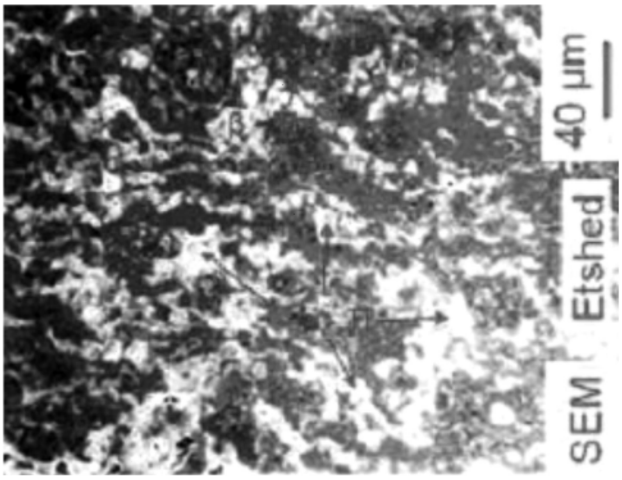

Figure 5: Shows a SEM micrograph of the coating at a higher magnification, in order to see more clearly the microstructure of the deposited coating

uniform in the cross-section of the coating, without micro- and macro-cracks.

The cross-section of the VPS-Ti coating, shown on the SEM microphotograph, clearly shows the two-phase structure of titanium, which consists of light fields of the α-Ti phase and dark-grey fields of the β-Ti phase marked with red arrows. Since the Ti powder particles were properly molten and the Ti droplets were correctly deformed when they contacted the substrate and previously deposited layers, the coating structure contains no interlamellar boundaries. The coating was formed by depositing one layer over another layer where the previously deposited and hardened lamellae serve as nucleation sites and promote the hardening of Ti droplets arriving on the substrate until the final coating thickness is achieved. Due to the rapid cooling of the deposited lamellae down to the substrate temperature, the phase transformation of the high-temperature β–Ti phase shifts at lower temperatures, so that a mixture of low-temperature α–Ti phase and high-temperature β–Ti phase is present in the coating structure. Characterisation of the VPS deposited layers of titanium showed that the layers have mechanical characteristics and microstructure, which fully enable the application of VPS-Ti coating in biomedicine as a bonding layer for the upper porous Ti coating in implant production.

4 CONCLUSIONS

In this paper, vacuum plasma spray (VPS) processes were used to deposit Ti coating layers. We analysed the mechanical characteristics of the coating and the microstructure of the coating, in both its deposited and etched forms, using OM and SEM microscopes, on the basis of which we have reached the following conclusions.

The vacuum plasma spray Ti coating had a mean microhardness value of 159 $HV_{0.3}$. The tensile strength of the Ti coating bond was 68 MPa. Roughening with corundum and cleaning the substrate surface with the transferred arch enabled good adhesion of the deposited layers of coatings, which was reflected in obtaining a high bond-strength value. The values of microhardness and tensile strength of the bond were correlated with their microstructures.

The structure of the coating shows that the evenly deposited layers on the substrate are composed of folded lamellae with good cohesion, because no interlamellar boundaries are observed. The microstructure of the VPS-Ti coating is homogeneous with a uniform distribution of the α-Ti and β-Ti phases throughout the coating layers. The existence of the high-temperature β-Ti phase in the coating is a consequence of the shift of the phase transformation to lower temperatures below the equilibrium temperature caused by the rapid cooling of the deposited lamellae.

VPS Ti coating had good mechanical and structural characteristics, bearing in mind that the goal was to make a Ti coating to be used as a bonding coating in the process of making implants.

Acknowledgment

This work was supported by The Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-68/2021-14/200287).

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