

MECHANICAL PROPERTIES AND MICROSTRUCTURES OF BIO-INERT LAYERS OF CHROME OXIDE COATINGS DEPOSITED BY THE APS PROCESS

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Summary:

Plasma spray Cr₂O₃ ceramic layers are used as a separate coating or as a supplement to bio-reactive organic composite ceramics Ca₁₀(PO₄)₆(OH)₂-Al₂O₃-ZrO₂-Cr₂O₃ and other bio-inert ceramics in composites of the types Al₂O₃-ZrO₂-SrO-Cr₂O₃-Y₂O₃, ZrO₂-TiO₂-Cr₂O₃ and TiO₂-Cr₂O₃ to increase the mechanical properties and resistance components of artificial joints on sliding abrasion and corrosion. This paper analyzes the influence of the plasma gun distance from the substrate on the mechanical properties and the microstructure of Cr₂O₃ layers deposited with the current of 40kW. The aim was to deposit layers with optimal characteristics that will enable the effective implementation of Cr₂O₃ layers on substrates of steel implants exposed to dry friction without lubrication and to corrosion of living tissues. The mechanical properties were tested by examining microhardness layers using the HV_{0.3} method and the strength was tested by tensile testing. The surface of powder particles was examined by SEM. The microstructures of layers were analyzed with the use of an optical microscope (OM) and a scanning electron microscope (SEM). The test results confirmed a possibility of effective application of bio-inert layers of Cr₂O₃ with other ceramics intended for the production of functional implants.

Keywords: substrates, microstructures, corrosion, ceramics.

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Introduction

The APS - atmospheric plasma spray process is one of the technologies used for the deposition of bio-reactive and bio-inert coatings on the surface of implants (Bag & Biswas, 2016, pp.117–128). For the majority of plasma spray coatings, argon (Ar) can be used as a carrier gas. However, for the melting of metal oxide powders in high temperature plasma, oxygen is often used as a carrier gas in order to minimize the decomposition of oxide powder (Morks & Akimoto, 2008, p.1). The degree of powder melting depends on the size and the particle size distribution, the spray system used for powder deposition and the coating deposition parameters (Wang & Shaw, 2007, pp.34), (Trifa et al, 2005, pp.54-69). In the previously published papers, it was found that the coating microstructure depends on the spraying conditions (Mrdak, 2017a, pp.30-44), (Mrdak, 2017b, pp.378-391). Layers of plasma sprayed oxides are widely used for improving resistance to wear, abrasion and corrosion. This includes a wide range of deposited materials of metal oxides. One such material is Cr_2O_3 oxide, which is characterized by high resistance to sliding wear and corrosion. Cr_2O_3 oxide produces chemically most inert thermal spray layers resistant to abrasion of all oxides produced in the Sulzer Metco company. Coatings are very dense and have a low coefficient of friction without the addition of lubricants. Because of that, they have found application in the process of implants production (Material Product Data Sheet, 2012). An important feature of Cr_2O_3 oxide is non-toxicity and biocompatibility. Due to strong bonds of valence electrons of chromium and oxygen atoms, Cr_2O_3 oxide is stable and bio-inert. The ceramic coating or Cr_2O_3 oxide film deposited on the surface of the implant passivates the alloy substrate surface (Co-Cr, Co-Cr-Mo, Ti-6Al-4V i Ti-6Al-7Nb) and prevents the migration of toxic metal ions from the substrate into the surrounding tissue (Ogwu et al, 2016). Cr_2O_3 oxide has a high resistance to corrosion in contact with living tissues and good tribological behavior during friction and abrasive wear (Pang et al, 2007, pp.3531-3537), (Szafarska & Iwaszko, 2012, pp.215-221). Depending on the applied thermal spray coating process, coatings have a variety of microstructures and properties. The homogeneity of the coating structure significantly affects its tribological behavior. However, plasma spray of the Cr_2O_3 oxide coating has the highest abrasion resistance in dry conditions and in lubrication conditions compared with Al_2O_3 and TiO_2 coatings (Cetinel et al, 2008, pp.259-265). During the process of powder melting in plasma, one part of Cr_2O_3 oxide is decomposed due to plasma high temperature. After the dual diagram Cr – O, Cr_2O_3 oxide occurs in several

crystalline phases such as Cr_3O_4 (29,1wt.%O), Cr_2O_3 (32wt.%O), CrO_2 (38,1wt.%O), Cr_5O_{12} (42,5wt.%O), Cr_6O_{15} (43,4wt.%O) and CrO_3 (48wt.%O) (ASM Handbook, 1992). Black $\alpha\text{-Cr}_2\text{O}_3$ oxide with a hexagonal lattice is used for deposition; the lattice basal planes are conveniently distributed in the coating thus giving good sliding properties. With the typical spraying parameters, Cr_2O_3 coating is somewhat under-stoichiometric, and its microstructure consists of the initial oxide type $\alpha\text{-Cr}_2\text{O}_3$, dark gray in color, and light gray Cr_3O_4 , CrO and CrO_2 oxides (Khanna & Bhat, 2006).

This paper presents the results of the influence of the plasma gun distance from the substrate on the mechanical properties and the microstructure of Cr_2O_3 layers. Powder is deposited on the metal surface at a distance of 90 mm, 100 mm and 110 mm. The adhesion strength, microhardness and microstructural characteristics of Cr_2O_3 coating were analysed; these coatings have layers of the best features which enable efficient implementation on the substrates in the conditions of bet lubrication friction and corrosion present on implants.

Materials and experimental details

For depositing layers of Cr_2O_3 , Sulzer Metco 106 NS powder was used; the powder particle surface is shown in SEM photomicrographs in Figure 1.

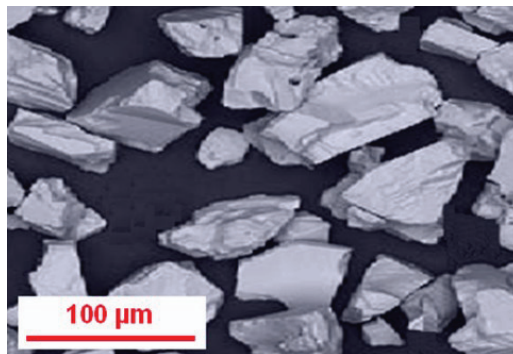


Figure 1 – (SEM) micrography of Cr_2O_3 powder particles
 Рис. 1 – (SEM) микрография частиц порошка Cr_2O_3
 Слика 1 – (SEM) микрографија честица праха Cr_2O_3

The applied powder was the $\alpha\text{-Cr}_2\text{O}_3$ modification produced by sintering and grinding to a granulation of $11\mu\text{m} - 90\mu\text{m}$ (Material Product Data Sheet, 2012). Cr_2O_3 coating layers are deposited on substrates of Č.4171 (X15Cr13 EN10027) steel in the thermally untreated condition. To

assess the microhardness and microstructure of coatings, the substrates had dimensions of 70x20x1.5mm. To assess the adhesion / cohesion strength of the layers, the substrate samples had dimensions Ø25x50 mm. The mechanical properties of layers were assessed in accordance with standard ASTM C633-1, 2008. The paper presents the minimum and maximum microhardness values $HV_{0.3}$ as well as the mean values of tensile bond strength.

The analysis of the microstructure of Cr_2O_3 layers was performed by an optical microscope. The assessment of content, distribution and size of micro pores was performed on five photos - OM at 200x magnification. The paper presents the mean value of the content of pores.

Cr_2O_3 powder was deposited at atmospheric pressure with a plasma spray of the Plasmadyne system. The SG-100 plasma gun which was used for powder deposition consisted of a cathode type K 1083A-129, an anode type A 2083-145 and a gas injector type GI 1083A-113. The plasma gas was a mixture of gases Ar / He and the power supply was up to 40kW. The powder deposition parameters are shown in Table 1. The deposited coatings had a thickness of 0.18 mm - 0.20mm.

Table 1 – Plasma spray parameters
Таблица 1 – Параметры плазменного напыления
Табела 1 – Плазма спреј параметри

Deposition parameters	Values		
Plasma current, I (A)	800	800	800
Plasma Voltage, U (V)	40	40	40
Primary plasma gas flow rate, Ar (l/min)	47	47	47
Secondary plasma gas flow rate, He (l/min)	12	12	12
Carrier gas flow rate, Ar (l/min)	6	6	6
Powder feed rate, (g/min)	40	40	40
Stand-off distance, (mm)	90	100	110

Results and Discussion

Distances of the plasma gun from the substrate had an important influence on the mechanical properties and microstructure of the deposited layers. The measured values of micro hardness and tensile strength of

Cr_2O_3 coatings depending on the distance of the plasma gun from the substrates are shown in Figures 2 and 3. The layers deposited with a minimum spray distance of 90 mm have the largest range of microhardness of $230\text{HV}_{0.3}$ and the lowest value of $1030\text{HV}_{0.3}$ to $1260\text{HV}_{0.3}$. The highest values of microhardness $1270\text{HV}_{0.3}$ to $1395\text{HV}_{0.3}$ occur in the layers deposited with the largest spray distance of 110 mm. The smallest microhardness range of $180\text{HV}_{0.3}$ was measured in these layers.

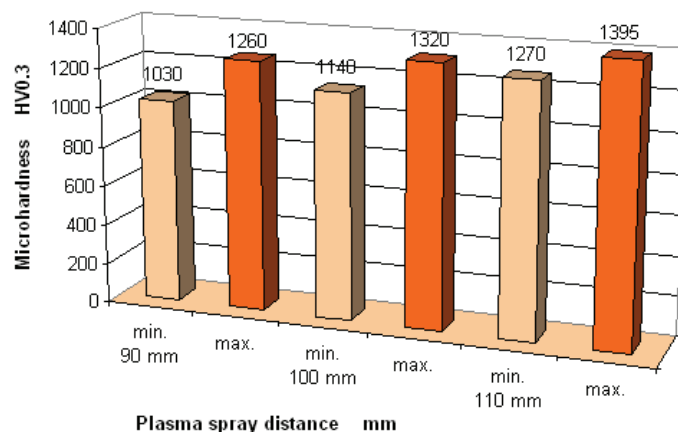


Figure 2 – Microhardness of Cr_2O_3 layers
 Рис. 2 – Микротвердость покрытия Cr_2O_3
 Слика 2 – Микротврдоћа Cr_2O_3 слојева

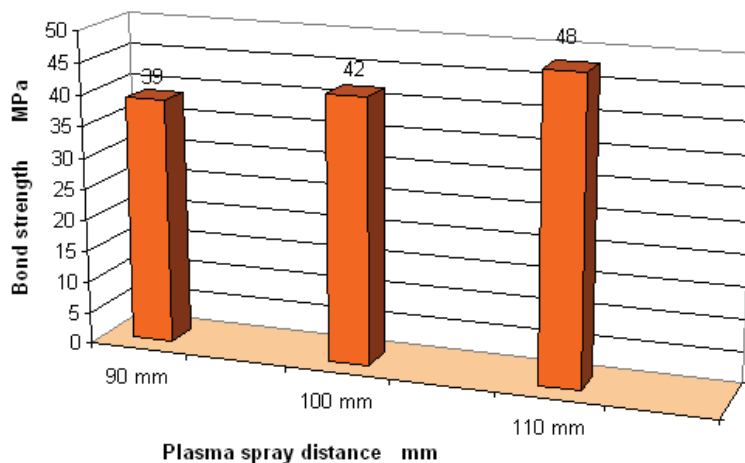


Figure 3 – Bond strength of Cr_2O_3 layers
 Рис. 3 – Прочность связи слоев покрытия Cr_2O_3
 Слика 3 – Чврстоћа споја Cr_2O_3 слојева

With the increase of the spray distance, powder particles melt better due to a longer stay in plasma. Better powder melting enabled the deposition of layers of higher density and higher adhesion / cohesion strength, which was confirmed by examining the deposited coatings.

The tensile strength of the bond of the Cr_2O_3 coating deposited with the smallest spray distance of 90 mm had the lowest value of the bond strength of 39 MPa. A smaller spray distance reduces the residence time of particles in plasma, therefore causing poorer melting of powder particles. The coating Cr_2O_3 deposited with the largest spray distance of 110 mm has the highest bond strength of 48 MPa. Due to a longer stay in plasma, powder particles have sufficient time to melt fully and bind tightly to the surface of the substrate and the particles from the previously deposited layers.

The metallographic analysis of Cr_2O_3 coatings showed a good bonding between the coating and the substrate; it also showed that there are no residual particles of corundum due to roughening at the interface. Micro and macro cracks are not observed along the interface; there is neither separation of the coating along the sample edges nor peeling off of the coatings from the substrates. There are neither micro/macro cracks nor unmelted powder particles in the deposited layers, which contributed to coatings having good adhesion / cohesion strength.

The microstructures of Cr_2O_3 coatings were in accordance with the mechanical characteristics of the coatings. The distance of the plasma gun from the substrate had a significant impact on the degree of melting and deformation of particles in collision with the substrate. Depending on the substrate distance, the layers of the deposited coatings had a different share, distribution and size of micro pores in the coating. Figure 4 shows the microstructure of Cr_2O_3 coatings deposited with a minimum distance of 90 mm from the substrate. The coating predictably had the highest proportion of micro pores, which resulted in the layers having minimum microhardness and adhesion strength. In the layers, there are coarse micro pores larger than 20 μm . The total share of micro pores was 9.3%. Because of smaller distances of the substrate and a shorter stay of powder particles in plasma, particles are half melted and, therefore, less deformed in collision with the substrate. As a result, the bonding surface between the deposited particles is reduced, the content of pores is increased as well as the presence of coarse pores which all leads to inferior mechanical properties of the coating.

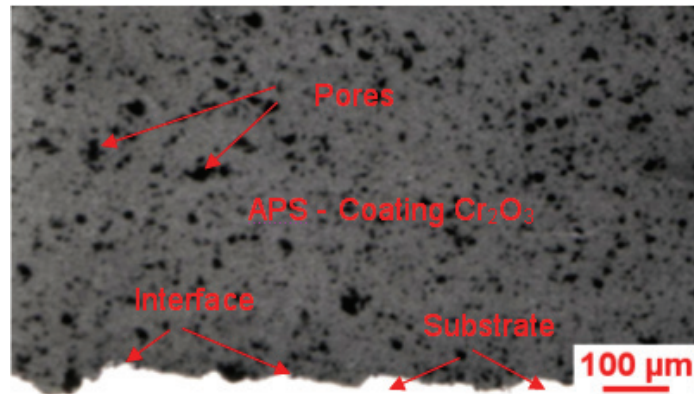


Figure 4 – Cr_2O_3 coating microstructure deposited from a distance of 90mm
 Рис. 4 – Микроструктура покрытия Cr_2O_3 , нанесенного с расстояния 90 мм
 Слика 4 – Микроструктура Cr_2O_3 превлаке са одстојањем 90 мм

Figures 5 and 6 show the microstructure of the Cr_2O_3 coating deposited on the substrate from a distance of 110 mm which had the best microstructure and mechanical properties.

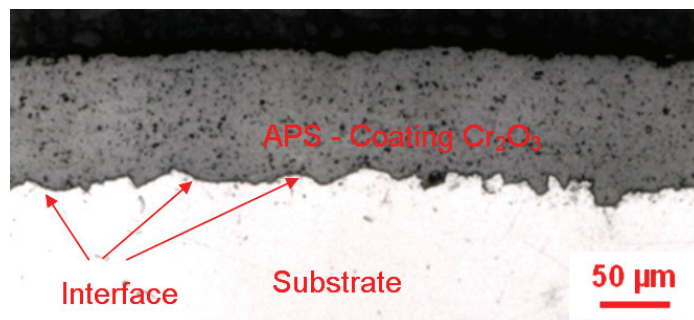


Figure 5 – Cr_2O_3 coating microstructure deposited from a distance of 110mm
 Рис. 5 – Микроструктура покрытия Cr_2O_3 , нанесенного с расстояния 110 мм
 Слика 5 – Микроструктура Cr_2O_3 превлаке са одстојањем 110 мм

A large distance from the substrate enabled the best melting of Cr_2O_3 powder particles and a uniform deposition of molten droplets on the surface of the substrate and previously deposited layers. In a collision with the substrate, droplets of molten particles spilled in a regular pattern and formed thin lamellae with a larger contact surface and a lower content of micro pores. The analysis of the micrograph showed that the Cr_2O_3 coating contains micro pores with an average content of 3.5%. The formed micro pores are black and of irregular shape.

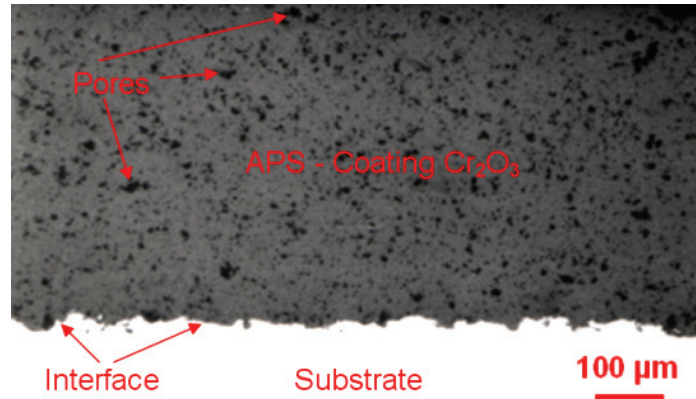


Figure 6 – Cr_2O_3 coating microstructure deposited from a distance of 110mm
 Рус. 6 – Микроструктура покрытия Cr_2O_3 , нанесенного с расстояния 110 мм
 Слика 6 – Микроструктура Cr_2O_3 превлаке са одстојањем 110 мм

The SEM micrograph shows the Cr_2O_3 coating with the best mechanical and structural characteristics (Figure 7).

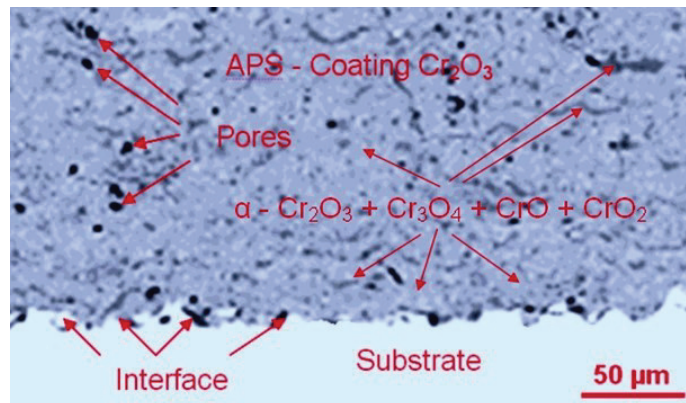


Figure 7 – (SEM) Cr_2O_3 coating microstructure deposited from a distance of 110 mm
 Рус. 7 – (SEM) Микроструктура покрытия Cr_2O_3 , нанесенного с расстояния 110 мм
 Слика 7 – (SEM) Микроструктура Cr_2O_3 превлаке депоноване са одстојањем 110 мм

Oxide lamellae of the deposited Cr_2O_3 coatings are clearly seen in the microstructure. Due to a partial decomposition of the initial dark gray phase of $\alpha\text{-Cr}_2\text{O}_3$ during plasma powder spraying, other types of oxides such as Cr_3O_4 , CrO and CrO_2 (light gray) are present in the microstructure of the coating (Schutz et al, 1991, p.649–669). Micro pores (black) can also be seen in the microstructure of the coating. Figure 8 shows a SEM micrograph of the Cr_2O_3 coating surface deposited from a distance of 110 mm and which had the best mechanical properties and the microstructure.

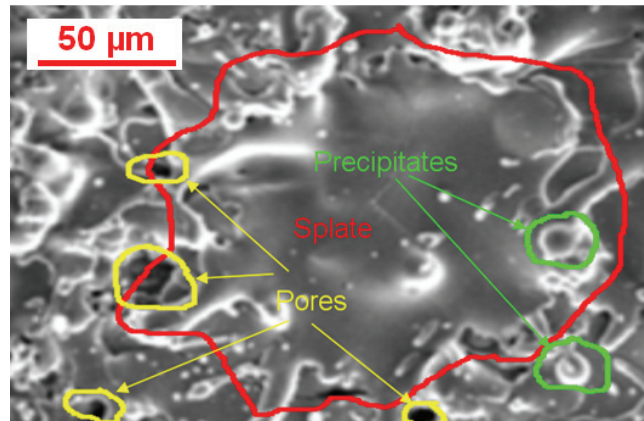


Figure 8 – (SEM) Surface morphology of the coatings deposited from a distance of 110 mm
 Рус. 8 – (SEM) Морфология поверхности покрытия, нанесенного с расстояния 110 мм
 Слика 8 – (SEM) Морфологија површине превлаке депоноване са одстојањем 110 мм

The coating surface shows complete melting and spreading of droplets of molten Cr_2O_3 particles on the previously deposited layer. The micrograph shows the surface of a molten and evenly distributed Cr_2O_3 droplet on the previously deposited layers (circled with a red line). The droplet of a molten powder particle formed a thin disk – splat of an approximately circular shape in a collision with the substrate surface. The deformed droplet, in a collision with the substrate, formed a regular shape, thus creating a good bond with the previously deposited layer. The evenly spilled particle has a lamellar structure in the cross section, as it can be seen in Figure 7.

In the microstructure, there are fine precipitates of approximately spherical size of $10\ \mu\text{m}$ formed by breaking off the edges of molten particles in a collision with the substrate. The SEM micrograph shows micro pores (black) up to $10\ \mu\text{m}$ circled in yellow.

Conclusion

The paper analyzes the mechanical properties and the microstructure of the deposited Cr_2O_3 layers depending on the distance of the substrate from the plasma gun, on the basis of which the following conclusions are derived.

The mechanical properties and the microstructure of Cr_2O_3 coating layers were in accordance with the conditions of the powder deposition. The microhardness values increase with increasing the substrate distance due to a longer stay of powder particles in plasma, which allows complete

powder melting. The layers deposited from the largest distance have the smallest range and highest microhardness values. These layers have proved to be the thickest. The mean content of micro pores in these layers was the lowest and amounted to 3.5%. Also, the maximum value of the adhesion strength of 48 MPa was found in the layers deposited from the largest distance of the substrate and with the lowest content of micro pores of 3.5%. The mechanical properties of Cr₂O₃ layers are in accordance with the microstructures.

In the microstructure of Cr₂O₃ layers, besides the initial oxide phase of α-Cr₂O₃ in dark gray, there are also present Cr₃O₄, CrO and CrO₂ oxides (light gray) due to partial decomposition of the initial oxide. Good mechanical and structural characteristics of Cr₂O₃ coating layers deposited on the substrate from a distance of 110mm allow its efficient application on steel implants with surfaces exposed to friction without lubrication as well as to corrosion.

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МЕХАНИЧЕСКИЕ ХАРАКТЕРИСТИКИ И МИКРОСТРУКТУРА
БИОИНЕРТНЫХ СЛОЕВ ХРОМОКСИДНЫХ ПОКРЫТИЙ,
НАНЕСЕННЫХ ВОЗДУШНО-ПЛАЗМЕННЫМ НАПЫЛЕНИЕМ

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ВИД СТАТЬИ: оригинальная научная статья

ЯЗЫК СТАТЬИ: английский

Резюме:

Метод плазменного напыления керамических Cr₂O₃ покрытий применяется как самостоятельное покрытие, так и в качестве дополнения к биоактивной органической композиционной керамике Ca₁₀(PO₄)₆(OH)₂-Al₂O₃-ZrO₂-Cr₂O₃ и к иным биоинертным

керамикам, создавая композиты типа $Al_2O_3-ZrO_2-SrO-Cr_2O_3-Y_2O_3$, $ZrO_2-TiO_2-Cr_2O_3$ и $TiO_2-Cr_2O_3$ с целью улучшения механических характеристик и повышения стойкости к износу и коррозии компонентов протеза сустава. В данной статье представлено каким образом расстояние между пистолетом для плазменного напыления и обрабатываемой поверхностью влияет на механические характеристики и микроструктуру Cr_2O_3 слоев покрытия, нанесенных при электромощности 40 кВт. Цель нанесения различных слоев заключалась в определении лучших характеристик, которые обеспечат эффективное применение покрытия Cr_2O_3 для подложек металлических имплантатов, подверженных сухому трению без смазки, а также коррозии живых тканей. Анализ механических характеристик покрытия проведен на основании испытаний микротвердости методом HV0.3 и прочности соединений методом растяжения. Структура слоев испытана методом оптической микроскопии (ОМ), а поверхность испытана методом электронной микрографии (SEM). На основании полученных характеристик установлено, что эффективное применение биоинертных слоев Cr_2O_3 возможно и в сочетании с другими керамическими покрытиями, предназначенными для изготовления функциональных имплантатов.

Ключевые слова: основа, микроструктура, коррозия, керамика.

МЕХАНИЧКА СВОЈСТВА И МИКРОСТРУКТУРЕ БИОИНЕРТНИХ СЛОЈЕВА ХРОМ-ОКСИДНИХ ПРЕВЛАКА ДЕПОНОВАНИХ APS-ПРОЦЕСОМ

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ОБЛАСТ: хемијске технологије
ВРСТА ЧЛАНКА: оригинални научни чланак
ЈЕЗИК ЧЛАНКА: енглески

Сажетак:

Плазма спреј керамички слојеви Cr_2O_3 користе се као засебна превлака или као додатак биореактивној органској композитној керамици $Ca_{10}(PO_4)_6(OH)_2-Al_2O_3-ZrO_2-Cr_2O_3$ и другим биоинертним керамикама, правећи компози типа $Al_2O_3-ZrO_2-SrO-Cr_2O_3-Y_2O_3$, $ZrO_2-TiO_2-Cr_2O_3$ и $TiO_2-Cr_2O_3$ за повећање механичких карактеристика и отпорности компоненти вештачког зглоба на хабање клизањем и корозију. У раду је анализиран утицај

одстојања плазма пиштоља од подлоге на механичке карактеристике и микроструктуру Cr_2O_3 слојева депонованих са снагом напајања од 40 kW. Циљ рада био је да се депонују слојеви оптималних карактеристика који ће омогућити ефикасну примену Cr_2O_3 слојева на подлогама челичних имплантата изложених сувом трењу без подмазивања и корозији живих ткива. Испитивање механичких карактеристика реализовано је испитивањем микротврдоће слојева методом $\text{HV}_{0.3}$ и чврстоће споја методом на затезање. Изглед површине честица праха испитан је методом SEM. Микроструктуре слојева анализирани су уз примену оптичког микроскопа (ОМ) и скенинг електронског микроскопа (СЕМ). Резултати испитивања потврдили су могућност ефикасне примене биоинертних слојева Cr_2O_3 са другим керамикама намењеним за израду функционалних имплантата.

Кључне речи: подлоге, микроструктура, корозија, керамика.

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