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Mechanical and structural features of Nb coating layers deposited on steel substrates in a vacuum chamber

ABSTRACT

In this paper analyzed was the influence of implementation of inert Ar gas and a mixture of inert plasma Ar / He gases in a vacuum chamber on the deposition of reactive niobium (Nb) powder. The aim of this paper was to deposit coating layers of high density, without oxide content, that will find application in the field of biomedicine. Detailed examination was performed of mechanical properties of microhardness using the $HV_{0.3}$ method, of tensile bond strength by tensile testing and of the microstructure of the coating layers in the deposited state and after etching. For etching a solution of nitric acid HNO_3 and hydrofluoric acid HF in a ratio of 1:1was used. It was found that inert gases, at low pressure prevent the reaction of gases with the metal droplets of molten Nb powder particles during the plasma spray deposition process. The density of the deposited coating in vacuum chamber is higher than that of coatings which are deposited at atmospheric pressure with reactive plasma gases N_2 and H_2. This is attributed to the elimination of thin oxide and nitride films at the interlamellar Nb contact, substantially increasing the ductility of the coating, eliminating the micro cracks through the deposited layers, which was confirmed by metallographic examination of samples. Tests have shown that VPS – Nb coating layers have mechanical properties and microstructure which completely enable the use of the coating on implants.

Keywords: *niobium, coatings, mechanical properties, vacuum, microhardness, bond strength*

1. INTRODUCTION

Process of deposition of metal and ceramic powders is mostly carried out at atmospheric pressure using the plasma spray process (APS) [1], but there is a variation where the plasma gun is enclosedin a vacuum chamber and the process of powder deposition is carried out under reduced pressure in an inert atmosphere, this is to reduce the reaction between the molten metal droplets and the gases. This process is used for deposition of metal powders that are reactive to gas [2]. Vacuum plasma spray technology can produce coatings with different density depending on use, which are homogeneous and very clean and free of oxides. Deposition of metal powder in a clean inert chamber greatly reduces the gas content in the deposited coating.

In fact, the gas content in the coating deposited in a vacuum chamber was virtually unchanged compared to the gas content in the powder. Reducing the gas content of the molten particles increases the materials deposit density. The coatings have a much greater bond strength compared to the APS coatings which were deposited at atmospheric pressure [3]. It is very important that the vacuum chamber, in the shortest possible time, reaches a vacuum of 10^{-3} mbar to successfully execute degassing of the chamber and avoid the reaction of gases with molten powder particles. In addition to the vacuum it is necessary to employ inert gases Ar and He of high purity, to be used as a shielding gas (Ar), andan arc gas (Ar) and a mixture of plasma gases (Ar/He). The VPS process allows the application ofa transferred arc with direct polarity for substrate surface cleaning and a transferred arc within direct polarity for heating of substrates, depending on the substrate material and the type of powder that is being deposited [2, 4, 5]. The microstructure of the VPS - Nb coating with a cubic centered crystal lattice is lamellar [6]. To see the lamellar structure of the coating the layers were etched with a solution of

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nitric acid HNO_3 and hydrofluoric acid HF in a ratio of 1: 1 [7]. Nitric acid HNO_3 together with Nb forms a thin film of niobium pentoxide Nb_2O_5 dark gray in color with a hexagonal crystal lattice [8]. Hydrofluoric acid HF reduces the niobium pentoxide Nb_2O_5 there in forming a thin film of niobium pentafluoride NbF_5 white in color with an orthorhombic lattice [7, 9]. Niobium is a metal of light gray color which is classified as a reactive metal that can easily electrochemically be oxidized. Pure Nb is characterized by a high melting temperature of 2468°C, a density of 8.55 g/cm^3, a good toughness in a cold atmosphere, a recrystallization temperature of 850°C to 1300°C depending on the degree of deformation, excellent corrosion resistance to liquid solutions and liquid metals, good biocompatibility, superconductivity, as well as a high absorption of carbon, oxygen, nitrogen and hydrogen, which is very dangerous due to embrittlement. Pure niobium is used for special applications in the chemical industry as a superconductor and for medical applications due to good biocompatibility. Nb has particularly been studied as a material for implants, and test results showed that this material has good biocompatibility and is viable for use as a biomaterial [6]. Surgical implants are usually made of metal materials, such as austenitic stainless steel, CoCr alloy and Ti and its alloys. Corrosion resistance of metal materials most commonly used as implants (austenitic stainless steel, cobalt - chromium alloy, titanium and titanium alloys) was based on the passivation of their surface with a thin layer of oxide [10] Among all metal materials, the most popular materials were of austenitic stainless steel because of their relatively low cost, ease of manufacture, and reasonable corrosion [11]. However, austenitic stainless steels cannot be used in long-term application because they are prone to local corrosion due to aggressive biological effects. The corrosion products include ions of iron, chrome, nickel and molybdenum, which accumulate in the tissues surrounding the implant, or are transported to distant parts of the body [12]. The need to reduce costs in the public health services influenced the use implants made of stainless steel as the most economical alternative. It is therefore important in the development of techniques to improve corrosion resistance and biocompatibility of this material. These facts contributed to designing and producing the desired coating materials for improving biocompatibility. One of the coatings which has been developed to reduce the concern of corrosion by physiological fluids and their biological activity and to improve the biocompatibility around dental implants is the Nb coating [13]. Deposition of Nb on implants made of stainless steel and titanium is one of the possible ways to improve the corrosion resistance in specific environments [14]. Studies have shown that biocompatible metal coatings such as Nb have a beneficial effect and the desired affect on the corrosion behavior of austenitic stainless steel 316L. This coating can improve the corrosion resistance and later can reduce the release of metal ions and their adverse effects on the surrounding tissues [15].

The aim of the paper was to use vacuum plasma spray technology to deposit Nb coating layers and for it to be applied in the process of implant production. In this study using the vacuum plasma spray (VPS) process the Nb coating layers were deposited to the steel substrates Č.4171 (X15Cr13 EN10027) in a thermally untreated condition. Microhardness, tensile bond strength and microstructure of the coating layers in the deposited and etched state were analyzedon the optical microscope (OM) and scanning electron microscope (SEM). Etching of the coating was carried out in a solution of nitric acid HNO_3 and hydrofluoric acid HF in a ratio of 1: 1. Based on the analysis, an assessment of the quality of the Nb coating was given as a potential candidate for application on implants made of stainless steel.

2. EXPERIMENTAL

2.1. Materials and experimental details of plasma spray coating deposition

For depositing niobium (Nb) coating layers a powder with particle size of 5 - 45 μm was used. Figure 1 shows the scanning electron micrographs (SEM) of the morphology of the Nb powder particles.

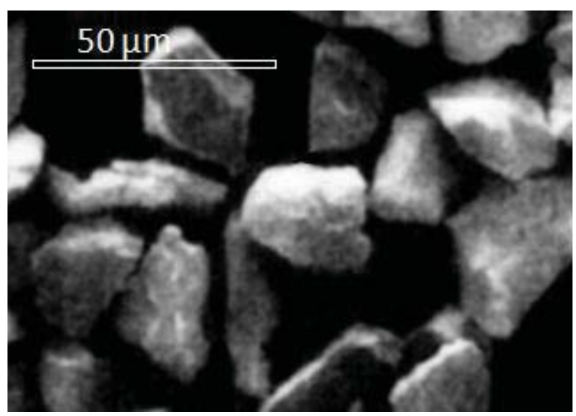

Figure 1. SEM: morphology of Nb powder particles

Slika 1. SEM: morfologija čestice praha Nb

The micrograph shows the irregular shape of the powder particles with angular and sharp edges. The samples with deposited layers of Nb coating for microhardness testing and microstructure assessing were made of steel Č.4171 (X15Cr13

EN10027) in a thermally untreated state 70x20x1.5mm in size. For testing of tensile bond strength the samples were made of the same material Ø25x50 mm in size according to the standard Pratt & Whitney [16]. Tests for mechanical and microstructural properties of Nb coating layers were carried out according to standard Pratt & Whitney [16]. Microhardness testing of the coating was done using the $HV_{0.3}$ method and the tensile bond strength by tensile testing. Microhardness testing was carried out in the direction along the lamellae, in the middle and at the ends of the sample. Five readings were done in three measuring locations, and this paper shows the mean value of microhardness. The test method for bond strength is tension testing. The study was conducted at room temperature with a tension speed of 1 mm/1min. Five specimens were used for the test, and this paper shows the mean value. Analysis of the share of micropores in the coating was carried out by examining 5 photos at 200X magnification. This paper presents the mean values of the share of micropores. Particle morphology was examined on the Scanning Electron Microscope (SEM). Microstructural analysis of the coating in deposited and etched state was performed on the optical microscope (OM) and scanning electron microscope (SEM). To observe the microstructure of the deposited layers in the coating, etching of the coating was done with a solution of nitric acid HNO_3 and hydrofluoric acid HFat a ratio of 1:1.

Deposition of Nb powder was carried out atlow pressure of inert gas (Ar) in the VPS system of the company Plasma. The VPS process is performed at a low pressure of Ar in very clear conditions and with the use of the transferred arc for cleaning and preheating the substrate. Figure 2 shows the VPS

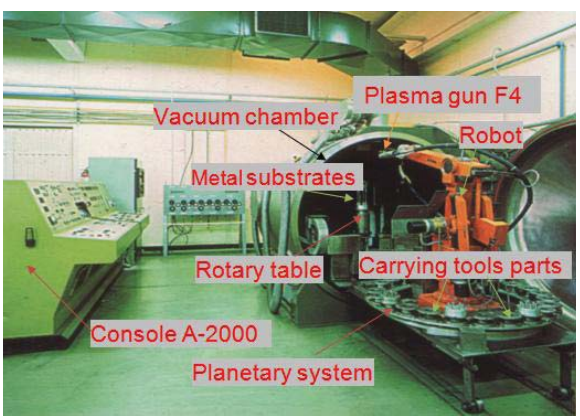

Figure 2. Vacuum plasma spray system

Figure 2. Vakuum plazma sprej sistem

system of the Plasma Technik AG company, which possesses an A - 2000 console and an F4 plasma gun. The powder deposition is usually performed with a mixture of Ar-He plasma gases at low pressure in the vacuum. In the vacuum chamber there are: a rotary table, planetary systems with 48 tools, a six-axis robot and an artificial hand. The manipulation system is designed to simultaneously rotate the tool and the operating parts around their axes. This complex movement allows uniform cleaning by the transferred arc and uniform powder depositing over the whole surface of the substrate. All procedures, being the parts of the VPS surface treatment process, must be carried out as quickly as possible. In order to obtain fast chamber vacuuming, a high pumping capacity is required. To achieve a chamber pressure of 1000 - 0.1 bar, a time of 5 minutes is necessary. The entire system is automated and programmed on the robot's microprocessor unit. All process parameters are entered into the program. The process of chamber vacuuming, the flow of plasma gases, the substrate cleaning, the powder flow, deposition, the substrate cooling and the vacuum chamber ventilation are fully synchronized by the program. Prior to the deposition of the powder roughening of the substrates was conducted with Al_2O_3 particles grain size of 0.7 - 1.5 mm. Cleaning the substrate surfaces and deposition of the powder was done with a mixture of plasma gases Ar-He. VPS parameters of Nb powder deposition on the samples are shown in Table 1. The coating was deposited at a thickness of 170-190μm.

Tabla 1. Parameters deposition powder Nb

Tabela 1. Parametri depozicije praha Nb

Parameters	Values	
	Cleaning arc	Spraying
Plasma current, I (A)	500	750
Plasma Voltage, V (U)	65	74
Primary plasma gas flow rate Ar, (l/min)	50	45
Secondary plasma gas flow rate He, (l/min)	10	120
Carrier gas flow rate Ar, (l/min)	--	3
Powder feed rate, (g/min)	--	35
Stand-off distance (mm)	280	270
Chamber pressure, (mbar)	40	120
Nozzle diameter, (mm)	8	8
Speed of the gun, (mm /s)	15	250

3. RESULTS AND DISCUSSIONI

3.1. Results of coatings testing

The mean microhardness value at the cross-section of layers of the Nb coating was $158HV_{0.3}$. The microhardness values of the Nb coating layers showed that the coating is soft and that at low pressure of the inert Ar gas and the inert plasma Ar / He gases it was not possible to form niobium oxide such as Nb_2O_5 or secondary metastable phases that cause brittleness of the coating. This was confirmed by analysis of the microstructure of the coating layers on an optical microscope (OM) and a scanning electron microscope (SEM). Tensile bond strength coatings depends on many parameters and some of the important ones are: surface roughness, sprayed material, spray parameters, used plasma gun, coating thickness, amount of unmelted particles and pores in the coating and coating thickness. For the coating Nb, during the tensile bond tests, the fracture occurred through the coating/substrate interface as well as and near the coating/substrate interface, which indicates we a good cohesion strength between the layers as shown in Figure 3.

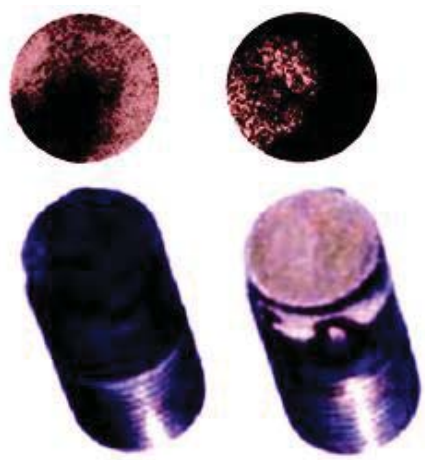

Figure 3. Mechanism of fracture coatings Nb

Slika 3. Mehanizam loma prevlake Nb

Bond tensile strength between the layers of Nb coating and substrates was 52MPa. Roughening and cleaning the surface of the substrates using a transferred arc has enabled good bonding of the melted Nb powder particles with the metal substrates, thus obtaining good bond tensile strength values. The microhardness values and bond tensile strength of the Nb coating layers were in accordance with the microstructure.

Figure 4 shows the microstructure of the Nb coatng layers in deposited state. At the interface between the substrate and the deposited coating layers there are no present discontinuities of layers on substrates or cracks and separation of the layers of the coating from the metal base. A good bond between the layers of coating and the substrates was achieved. The micrograph shows that the coating made a good bond with the substrate. Between the melted and deposited Nb powder particles a good cohesive bond was achieved, due to which there were no observed interlamellar boundaries or micro cracks.

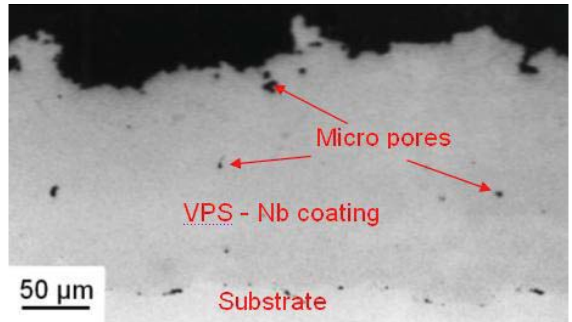

Figure 4. Microstructure of Nb coatings deposited in the state

Slika 4. Mikrostruktura Nb prevlake u deponovanom stanju

In the microstructure of the niobium coating there were no observed lamellae of secondary metastable phases or Nb_2O_5 oxide. This indicates that the use of a mixture of inert plasma Ar / He gases at low pressure of the inert Ar gas eliminated oxidation of molten Nbdroplets. The microstructure of the Nb coating in deposited state is single-phased of a light gray color with a centered cubic crystal lattice. In the structure of the coating micro pores can be seen black in color marked by red arrows. The share of micro pores in the layers of Nb coating was below 1%.

In Figures 5 and 6, shown are microstructures of vacuum plasma spray Nb coating after etching in a solution of nitric acid HNO_3 and hydrofluoric acid HF in a ratio of 1:1. By etching of Nb coating layers, in the microstructure boundaries appeared between the lamellae of well melted particles and semi-melted powder particles. Nitric acid HNO_3 reacted with Nb and on the surface of the cross section of the coating formed a thin film of niobium pentoxide Nb_2O_5, dark gray with a hexagonal crystal lattice as follows:

$$6\ Nb + 10\ HNO_3 = 3\ Nb_2O_5 + 10\ NO + 5H_2O$$

In Figures 5 and 6 shown are dark gray fields of niobium pentoxide Nb_2O_5 marked with red arrows. Niobium pentoxide Nb_2O_5 is unstable in hydrofluoric acid HF, causing reduction and formation of a thin film of niobium pentafluoride NbF_5. Pentafluoride NbF_5 is also formed by the reaction of pure Nb with nitric acid HNO_3 and hydrofluoric acid as follows:

$$Nb_2O_5 + 10\ HF = 2\ NbF_5 + 5\ H_2O$$

$$3Nb + 5\ HNO_3 + 15\ HF = 3\ NbF_5 + 5\ NO + 10\ H_2O$$

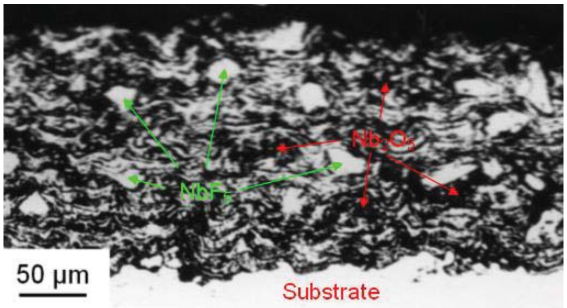

Figure 5. Microstructure of Nb coatings in etched state

Slika 5. Mikrostruktura Nb prevlake u nagrizenom stanju

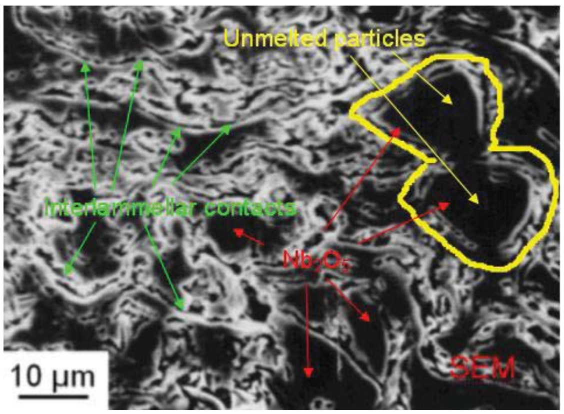

Figure 6. SEM Microstructure of Nb coatings in etched state

Slika 6. SEM mikrostruktura Nb prevlake u nagrizenom stanju

Niobium pentafluoride NbF_5 is white in color with an orthorhombic lattice marked with green arrows in the micrographs.

SEM micrograph 6 shows the microstructure of the Nb coating after etching. In the micrograph clearly can be seen the dark gray fields of the thin film of niobium pentoxide Nb_2O_5 formed on the surface of the cross section of the coating after etching. In the microstructure seen can be the lamellae, interlamellar contacts marked by green arrows and the unmelted powder particles circled and marked with yellow arrows. The unmelted powder particles in the microstructure of the coating confirmed that for the deposition of powderthe powder usedwas of irregular shape with angular grains.

4. CONCLUSION

For this paperlayers of Nb coating were deposited using the vacuum plasma spray process. Analyzed were the mechanical properties and microstructure of the coatings in deposited state and etched in the reagent HNO_3:HF in a ratio 1:1, based on which the following conclusions we made.

The Nb coating had a mean value of microhardness of $158HV_{0.3}$ and tensile bond strength of 52MPa. Roughening and cleaning of the substrate surface with a transferred arc allowed better bonding of melted powder particles to the substrate, which resulted in obtaining good tensile bond strength values. Mechanical properties of the Nb coating were correlated with the microstructures.

The microstructure of the Nb coating in deposited state was single-phased. In the microstructure of the coating present is a Nb phase with a centered cubic crystal lattice. In the microstructure of the coating there were no present secondary or oxide phases or micro cracks that decrease toughness and cause embrittlement of the coating. The quantity of micropores in the coating was less than 1%.

The microstructure of the Nb coating, after etching, was lamellar. On the surface of the cross-section of the coating, in the microstructure, lamellae of formed niobium pentoxide Nb_2O_5, dark gray and niobium pentafluoride NbF_5, white can be seen. On the basis of the formed phases, the microstructure showed that the deposited coating layers were uniformly deposited and rather homogenous with an insignificant share of fine unmelted powder particles.

The Nb coating had good mechanical properties and microstructure, bearing in mind that the aim was depositing Nb coatings that would, based on mechanical and structural properties find biomedical applications in the process of implant production.

Acknowledgments

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IZVOD

MEHANIČKE I STRUKTURNE KARAKTERISTIKE SLOJEVA PREVLAKE Nb DEPONOVANE U VAKUUMU

U ovom radu ispitan je uticaj primene inertnog gasa Ar i mešavine inertnih plazma gasova Ar / He u vakuum komori na depoziciju reaktivnog praha niobijuma (Nb). Cilj rada je bio da se deponuju slojevi prevlake visoke gustine bez sadržaja oksida koji će naći primenu u oblasti biomedicine. Izvršena su detaljna ispitavanja mehaničkih karakteristika mikrotvrdoće metodom $HV_{0.3}$ i zatezne čvrstoće spoja ispitivanjem na zatezanje i mikrostrukture slojeva prevlake u deponovanom stanju i posle nagrizanja. Za nagrizanje se koristio rastvor azotne kiseline HNO_3 i fluorovodoniče kiseline HF u odnosu 1 : 1. Utvrđeno je da inertni gasovi na niskom pritisku sprečavaju reakciju gasova sa metalnim kapima istopljenih čestica praha Nb tokom plazma sprej depozicije. Gustina deponovane prevlake u vakuumu je veća u odnosu na prevlake koje se deponuju na atmosferskom pritisku sa reaktivnim plazma gasovima N_2 i H_2. Ovo se pripisuje eliminisanju tankih filmova oksida i nitrida na međulamelarnim kontaktnim Nb, što značajno povećava duktilnost prevlake, eliminišući mikro pukotine kroz deponovane slojeve, što su potvrdila metalografska ispitivanja uzoraka. Ispitivanja su pokazala da slojevi VPS - Nb prevlake imaju mehaničke karakteristike i mikrostrukturu, koje u potpunosti omogućavaju primenu prevlake na implantima.

Ključne reči: *niobijum, prevlaka, mehanička svojstva, vakuum, mikrotvrdoća, čvrstoća spoja.*

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