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Mechanical properties and microstructure of the $ZrO_2$5CaO/NiCrAl coating system

ABSTRACT

$ZrO_2$5CaO is a versatile class of material that can be sintered or plasma spray deposited in combination with other materials on the implant substrate. Due to brittleness the organic ceramic hydroxyapatite $Ca_{10}(PO_4)_6$ $(OH)_2$ - (HA) is not suitable for use as a separate material in the process of making implants. In order to improve the mechanical characteristics and osteoconductivity, to HA ceramics added are dual systems of oxide solid solutions, of which one is also $ZrO_2$5CaO. Ceramics ZrO_2-CaO(95%-5%) as a biomaterial facilitates osteoconductivity in new bone formation around the implant. This paper represents the need to develop a system of $ZrO_2$5CaO/NiCrAl coatings that will with their mechanical and structural characteristics find application on implant parts. In this context, using the atmospheric plasma spray process deposited were the $ZrO_2$5CaO/NiCrAl coatings system on stainless steel substrates X15Cr13 (EN 1.4024). Analysis of the morphology of the powder particles and the surface of the $ZrO_2$5CaO coatings was carried out on the SEM. The microstructure of the layers of the coatings system was analyzed on the OM. Mechanical properties of the coating were determined by examining the microhardness using the $HV_{0.3}$ method and bond strength by tensile testing according to the standard (ASTMC633-1).

***Keywords**: APS - atmospheric plasma spraying, NiCrAl, $ZrO_2$5CaO, microstructure, interface, microhardness, bond strength.*

1. INTRODUCTION

Calcium phosphate ceramics $Ca_{10}(PO_4)_6(OH)_2$ - HA is in its composition and structure similar to bone mineral and represents the basic ceramicsin the process of production of biomedical coatings to be applied to implants. It has excellent biocompatibility, which allows the growth of bone cells on its surface [1]. Since HA is a brittle ceramics it is not suitable to be applied as a separate coating on constructional implants. The way to overcome this problem is to add bioinert ceramics, which would provide the necessary mechanical strength and toughness for the coating. For this purpose used as a supplement is oxide ceramics ZrO_2 which with its physical, chemical and biological properties has made great progress in the process of manufacture of the latest generation of implants [2,3]. Good dimensional stability of ZrO_2 ceramics, its mechanical strength and toughness together with the Young's modulus has the same order of magnitude as alloys of stainless steels which are used as a substrate for the production of implants. Today biomaterial ZrO_2 is considered as one of the most important in orthopedic surgery. In the stages of development of new generations of implants for biomedical applications several solid solutions (ZrO_2-MgO, ZrO_2-CaO, ZrO_2-Y_2O_3) were tested, as well as other types of oxides such as Al_2O_3 and TiO_2. Calcium oxide (CaO) is the most widely used to stabilize the zirconium oxide because of its low price.

For complete stabilization of zirconium oxide, more than 16mol% CaO (7.9% wt.%CaO) is needed [4]. Moreover recent studies found that a coating of ZrO_2-CaO (95%-5wt.%) as a bioactive material facilitates new bone formation, that is, accelerates the process of osteoconductivity [5]. The CaO-ZrO_2 coating in combination with the NiMoAl bond coating is used for deposition with the

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plasma process, on Ti substrate surfaces before binding of titanium-porcelain for restoration of teeth in dentistry [6]. The bond layer improves adhesion between the substrate and the top ceramic layer. Modified HA coatings with ZrO_2 solid solutions are successfully used today in orthopedics and dentistry with very encouraging results [7]. Today plasma spraying is a standard method for production of biomedical coatings based on HA inorganic ceramics and metals Ti, Nb and Ta [3,8-10]. This technological process allows high speed powder deposition, which results in high production for coating of the implant substrates [11]. It is very important during the spray coating to avoid transformation of the tetragonal to the monoclinic phase. The coating should not, in its structure have a monoclinic phase due to volumetric changes. This is avoided by rapid cooling of the deposited particles and the substrate with compressed air. Low thermal conductivity of zirconium oxide prevents complete heating of powder particles in the plasma, due to which the particle cores are not melted. This causes lesspreading of particles that collide with the substrate making inter-lamellar porosity in the range of 2% - 10% and microcracks [12].

This study investigates the mechanical properties and microstructure of the $ZrO_2$5CaO / NiCrAl coatings system deposited by atmospheric plasma spraying on a steel substrate X15Cr13 made of stainless steel (EN 1.4024). The aim of the study was to produce coating layers based on ZrO_2 ceramics partially stabilized with CaO with structural and mechanical properties which will find use on implants. On the basis of analysis the ZrO_2-CaO coating has good mechanical properties and microstructure which make it suitable for application on implants.

2. EXSPERIMENTAL PART

2.1. Materials and experimental details of plasma spray coatings deposition

For the deposition of $ZrO_2$5CaO/NiCrAl coatings systems applied were powders of the Sulcer Metco company, marked Metco443NS and Metco 201B-NS-1. The powder Metco 201B-NS-1($ZrO_2$5CaO) was produced by the method of melting, casting and grinding to the granulation of 25 μm - 90 μm. Figure 1 shows the SEM micrograph of the morphology of the $ZrO_2$5CaO powder particles. The ground powder particles are irregularly shaped with sharp edges [13].

The substrate material for deposition of coatings was stainless steel X15Cr13 (EN 1.4024).

Testing the mechanical characteristics of the coatings system was carried out according to standard [14]. For testing microhardness and analysis of microstructure of the layers, samples 70x20x1.5mm in size were made, and for testing of bond strength specimens Ø25x50 mm in size were made. Microhardnesses of the coatings were examined by the $HV_{0.3}$ method and the bond strength by tension method. Measurement of microhardness of layers was carried out by reading five values in the direction along the lamellae in the middle and at the ends of the samples. The paper presents the min. and max. values. The bond strength of the layers was tested on five specimens at room temperature, and the paper shows the average value.

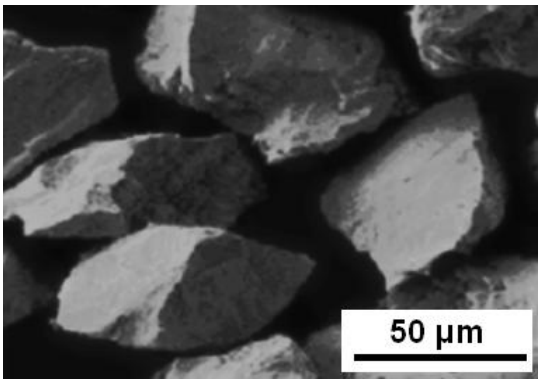

Figure 1. (SEM) micrograph of the $ZrO_2$5CaO powder particles

Slika 1. (SEM) mikrografija čestica praha $ZrO_2$5CaO

The microstructure of the layers, and the content of pores in the coating layers were analyzed on an optical microscope (OM). The paper presents the mean values of content of pores in the coatings.

The powders were deposited at atmospheric pressure using the APS system of the company Plasmadyne and the plasma SG-100 gun. Parts that made up the plasma gun are the K 1083-129 type cathode, the A 2083-175 type anode and a gas injector type GI 1083A-130. As the plasma gas used was a mixture of Ar and He gases, and for deposition a power supplyto the plant up to 40 kW. The parameters of the deposition of powders are shown in Table 1.

Table 1. Powders deposition parameters

Tabela 1. Parametri depozicije praha

Parameters	Metco 443NS	Metco 201B-NS-1
Plasma current, I (A)	800	700
Plasma voltage, U (V)	36	35
Primary Ar plasma gas flow, l/min	47	47
Secondary He plasma gas flow, l/min	12	12
Carrier Ar gas flow, l/min	7	6
Powder flow rate, g/min	50	45
Substrate distance, mm	90	110

Two groups of samples were made with different thicknesses of the bond and ceramic coatings, in order to determine how the thicknesses of the coatings affect the bond tensile strength. The first group was made with thicknesses of bond coating 80-100 µm/380-400 µm ceramic coating, and a second group of samples with coating thicknesses bond coating 20µm/100 µm ceramic coating.

3. RESULTS AND DISCUSSION

3.1. Results of coatings testing

The values of microhardness of the $ZrO_2$5CaO/ NiCrAl coatings system are shown in Figure 2. The NiCrAl bond coatings had a range of microhardness from 235 $HV_{0.3}$ to 268 $HV_{0.3}$. Values were uniform at the coating cross-section, indicating that the layers have a low content of pores. The ceramic coatings also had an even distribution of microhardness from 539 $HV_{0.3}$ to 607 $HV_{0.3}$. The greater range of microhardnessin the ceramic layers is caused by the high melting temperature of the ceramic particles, which are less plastically deformed in collision with the substrate. Distribution of microhardness of the coating layers at the cross section of the samples were in accordance with the content of pores and microstructures, as confirmed by analysis of the micrographs.

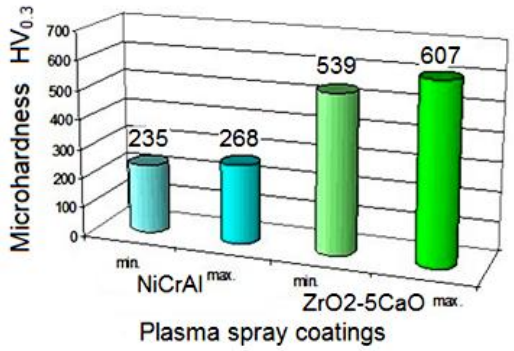

Figure 2. Microhardness of $ZrO_2$5CaO/NiCrAl coating

Slika 2. Mikrotvrdoća prevlake $ZrO_2$5CaO/NiCrAl

The $ZrO_2$5CaO/NiCrAl coatings system with thicknesses of the bond coating 80 - 100 µm/380 - 400 µm of the ceramic coating had a mean bond tensile strength value of 35MPa. For a coating system with smaller thickness such as, bond coating of 20µm/100µm for ceramic coating, the average value of tensile strength is substantially higher and is 56 MPa. Tensile strength of the thinner coatings system is as expected, higher, because the deposition of thin layers brings less stress into the ceramic coatings. With increasing thickness of the ceramic coating increases the content of residual stresses in the coating which reduce adhesion and cohesive strength of the coating. The bond tensile strength values of the $ZrO_2$5CaO/NiCrAl coatings system are in accordance with the microstructure of the deposited layers.

Figures 3 and 4 show the microstructure of the $ZrO_2$5CaO/NiCrAl coatings system with thicknesses of the bond coating 80 - 100 µm/380 - 400 µm of the ceramic coating, and in Figure 5 with the thicknesses of the bond coating 20 µm/100 µm of the ceramic coating. On the micrographs clearly observed on the cross section are the boundary lines at the joining of the substrate / NiCrAl bond coating and the NiCrAl bond coating / upper $ZrO_2$5CaO ceramic coating. At the boundary lines between substrate / bond coating and bond coating / ceramic coating there are no anomalies such as: discontinuity of deposited layers on the substrate, macro and micro cracks, delamination and flaking of the coating from the substrate.

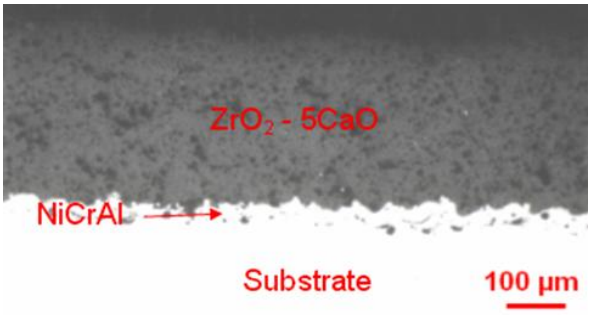

Figure 3. The microstructure of $ZrO_2$5CaO/NiCrAl coatings

Slika 3. Mikrostruktura prevlake $ZrO_2$5CaO/NiCrAl

Analysis of micrographs determined that in the NiCrAl bond coating layers the content of micro pores was small with a content of 1.5%. In the layers of $ZrO_2$5CaO ceramic coating the content of micro pores was 8%. In Figures 4 and 5 the micro pores in the ceramic coating are black in color marked with red arrows.

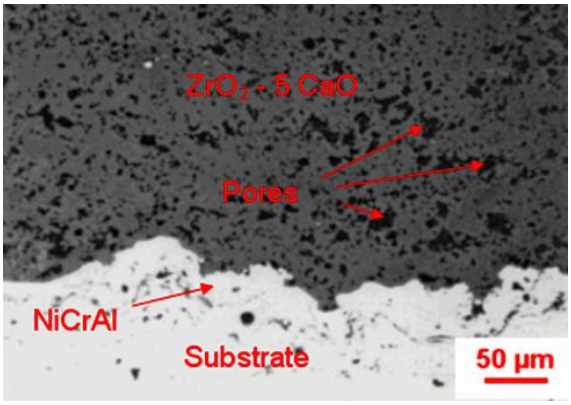

Figure 4. The microstructure of ZrO25CaO/NiCrAl coatings

Slika 4. Mikrostruktura prevlake $ZrO_2$5CaO/NiCrAl

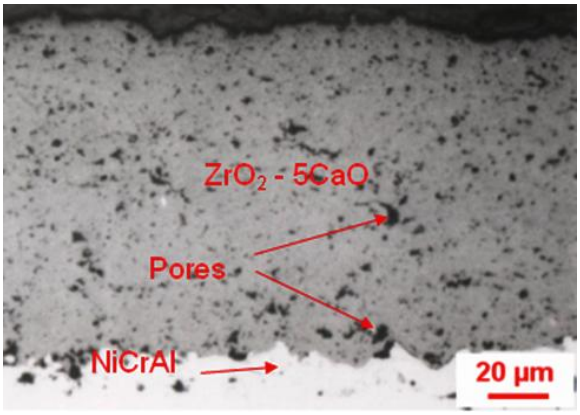

Figure 5. The microstructure of $ZrO_2$5CaO/NiCrAl coatings

Slika 5. Mikrostruktura prevlake $ZrO_2$5CaO/NiCrAl

The $ZrO_2$5CaO ceramic coating is uniformly deposited on the bond coating layers. Through the ceramic layers at the cross-section there are no observed unmelted particles, micro or macro cracks.

Figure 6 shows the microstructure of the NiCrAl bond coating deposited with a thickness of 100 µm. The structure of the coating is lamellar, they consist of a γ-Ni(Cr,Al) solid solution of a light gray color. Along the boundaries of the solid solution lamellae separated are lamellae of oxide phases: NiO, $NiCr_2O_3$, Cr_2O_3 and CrO_3, which are dark gray [12]. In the layers of the coating present are micro pores black in color, while there are no unmeleted particles or precipitates detected.

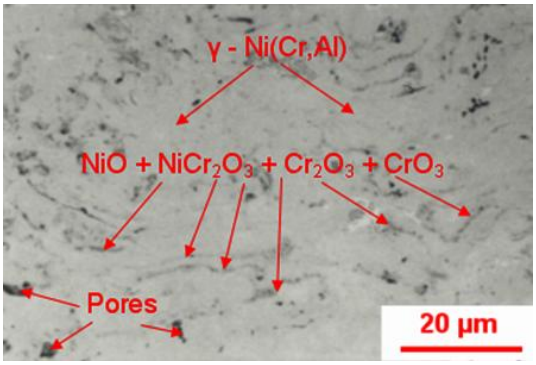

Figure 6. The microstructure of $ZrO_2$5CaO/NiCrAl coatings

Slika 6. Mikrostruktura prevlake $ZrO_2$5CaO/NiCrAl

In Figure 7 the SEM micrograph shows the morphology of the deposited $ZrO_2$5CaO ceramic particle on the surface of the coating. Analysis of the surface morphology shows limited plastic deformation of the $ZrO_2$5CaO particle onto the previously deposited ceramic layer. Due to the high melting point the particles in the coreare semi-melted and are less deformed in collision with the substrate. On the surface of one deposited particle fine precipitates from 3 µm to 8 µm in size circled in green can be seen. On the surface micro-cracks can be seen, indicated by yellow arrows, which extend from the surface towards the inner layers in depth of the coating. Micro cracks are the result of faster cooling of the particles on the surface with compressed air in relation to the deposited layers underneath which cooled more slowly and oppose the contracting of particles which harden on the surface of the coating. The inner layers of the ceramic coating due to higher temperatures are exposed to yield stress, and the particle which is contracting and solidifying is exposed to the compressive stresses[12].

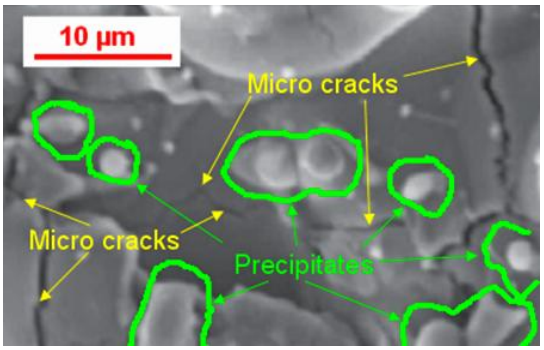

Figure 7. (SEM) Surface morphology of the $ZrO_2$5CaO coating

Slika 7. (SEM) morfologija površine prevlake $ZrO_2$5CaO

4. CONCLUSIONS

In this paper, analyzed were the mechanical properties and microstructure of the $ZrO_2$5CaO/NiCrAl coatings system on the basis of which the following conclusions were made.

Microhardnesses of the NiCrAl bond coating are uniform with a range of 235-268$HV_{0.3}$. The layers of ceramic coating had microhardness distribution in a range of 539-607$HV_{0.3}$. The content of micro pores in the NiCrAl bond coatings was 1.5%, and in the $ZrO_2$5CaO ceramic coatings the pore content was 8%. Tensile strength of the thinner coating system was the highest at 56 MPa, because with increasing thickness of the ceramic coating increases the content of residual stresses which reduce the adhesion / cohesion strength of the coating.

The microstructure of the bond coatings is lamellar, which consist of a γ-Ni(Cr,Al) solid solution and inter-oxide phases: NiO, $NiCr_2O_3$, Cr_2O_3, CrO_3. In the layers present are micro pores black in color. The upper $ZrO_2$5CaO ceramic coating is uniformly deposited on the bond coatings layers in which there are no unmelted particles or cracks present.

The deposited $ZrO_2$5CaO/NiCrAl coatings systems can be, on the basis of the mechanical and

structural features, applied with other ceramic materials for the preparation of a coatings system in the field of biomedicine.

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IZVOD

MEHANIČKE OSOBINE I MIKROSTRUKTURA SISTEMA PREVLAKA $ZrO_2$5CaO/NiCrAl

$ZrO_2$5CaO je višenamenska klasa materijala koja može da se sinteruje ili plazma sprej deponuje u kombinaciji sa drugim materijalima na podlogama implantata. Zbog krtosti organska keramika hidroksiapatit $Ca_{10}(PO_4)_6(OH)_2$ - (HA) nije pogodna za primenu kao zaseban materijal u procesu izrade implantata. U cilju poboljšanja osteokonduktivnosti i mehaničkih karakteristika, keramici HA se dodavaju dvojni sistemi čvrstih rastvora oksida od kojih je jedan i $ZrO_2$5CaO. Keramika ZrO_2-CaO(95%-5%) kao biomaterijal olakšava osteokonduktivnost u novom formiranju kostiju oko implantata. Ovaj rad predstavlja potrebu za izradom sistema $ZrO_2$5CaO/NiCrAl prevlaka koje će po svojim mehaničkim i strukturnim karakteristikama naći primenu na delovima implantata. U tom kontekstu atmosferskim plazma sprej procesom deponovan je sistem prevlaka $ZrO_2$5CaO/NiCrAl na čeličnim podlogama od nerđajućeg čelika X15Cr13 (EN 1.4024). Analiza morfologije čestica praha i površine prevlaka $ZrO_2$5CaO sprovedena je na SEM-u. Mikrostruktura slojeva sistema prevlaka ispitana je na OM-u. Mehaničke karakteristike prevlaka su sprovedene ispitivanjem mikrotvrdoće metodom $HV_{0.3}$ i čvrstoće spoja ispitivanjem na zatezanje po standardu (ASTMC633-1).

***Ključne reči**: APS - atmosferski plazma spreing, NiCrAl, $ZrO_2$5CaO, mikrostruktura, interfejs, mikrotvrdoća, čvrstoća spoja.*

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