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$5CaO coatings was carried out on the SEM. The microstructure of the layers of the coatings system was analyzed on the OM. Mechanical properties of the coating were determined by examining the microhardness using the HV$_{0,5}$ method and bond strength by tensile testing according to the standard (ASTM C633-1).

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 ceramicin 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$_2$O$_3$) were tested, as well as other types of oxides such as Al$_2$O$_3$ 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
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 ZrO₂ 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 monclinic 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 less spreading 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 ZrO₂5CaO / 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 ZrO₂ ceramics partially stabilized with CaO with structural and mechanical properties which will find use on implants. On the basis of analysis the ZrO₂-CaO coating has good mechanical properties and microstructure which make it suitable for application on implants.

2. EXPERIMENTAL PART
2.1. Materials and experimental details of plasma spray coatings deposition

For the deposition of ZrO₂5CaO/NiCrAl coatings systems applied were powders of the Sulcer Metco company, marked Metco443NS and Metco 201B-NS-1. The powder Metco 201B-NS-1(ZrO₂5CaO) 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 ZrO₂5CaO 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 HV₀.₅₀ 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 ZrO₂5CaO powder particles

Slika 1. (SEM) mikrografija čestica praha ZrO₂5CaO

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 supply to the plant up to 40 kW. The parameters of the deposition of powders are shown in Table 1.

Table 1. Powders deposition parameters

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

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.

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$5CaO ceramic coating the content of micro pores was 8%. In Figures 4 and 5 the micro pores in the ceramic coating are black in color marked with red arrows.
The ZrO$_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$_2$O$_3$, Cr$_2$O$_3$ 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 unmelted particles or precipitates detected.

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.

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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5. REFERENCES


IZVOD

MEHANIČKE OSOBINE I MIKROSTRUKTURA SISTEMA PREVLAKA ZrO25CaO/NiCrAl

ZrO25CaO je višenamenska klasa materijala koja može da se sinteruje ili plazma sprej deponuje u kombinaciji sa drugim materijalima na podlogama implantata. Zbog krstosti organska keramika hidroksiapatit Ca10(PO4)6(OH)2 - (HA) nije pogodna za primenu kao zaseban materijal u procesu izrade implantata. U cilju poboljšanja osteokonduktivnosti i mehaničkih karakteristika, keramika HA se dodajuvoj sistemi čvrstih rastvora oksida od kojih je jedan i ZrO25CaO. Keramika ZrO2-CaO (95%-5%) kao biomaterial olakšava osteokonduktivnost u novom formiranju kostiju oko implantata. U tom kontekstu atmosferskih plazma sprej procesom deponovan je sistem prevlaka ZrO25CaO/NiCrAl na čeličnim podlogama od nerđajućeg čelika X15Cr13 (EN 1.4024). Analiza morfologije čestica praha i površine prevlaka ZrO25CaO 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 čvrstoći spoja ispitivanjem na zatezanje po standardu (ASTM6333-1).


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