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## Characterization of zirconium oxide coating stabilized with cerium and yttrium oxide deposited on the bonding coating nickel chromium aluminum cobalt yttrium oxide

### ABSTRACT

Zirconium dioxide  $ZrO_2$  is used as a basic material for thermal barriers and as a biomaterial for manufacturing parts for hip implants in orthopedic surgery and in dentistry for making crowns. Use of  $ZrO_2$  ceramics as an insulating material and biomaterial is due to its good chemical and dimensional stability, mechanical strength, toughness and elastic modulus. The aim of this study was to analyze the characteristics of zirconium oxide coating of stabilized cerium and yttrium oxide deposited by atmospheric plasma spraying (APS) process on the bond coating of nickel chromium cobalt yttrium oxide. Coatings were deposited on cold substrates and on substrates preheated to  $180^\circ C$ . Composite powder nickel chromium/aluminum/cobalt/yttrium oxide was used for the production of bond layers and for the ceramic layers zirconium oxide stabilized with cerium and yttrium oxide powder. Testing the quality of coatings was done by measuring microhardness of layers using the HV method and for bond tensile strength of the coating system tensile testing was applied. Metallographic evaluation of the share of pores in the bond and ceramic layers was performed with image analysis - processing of images from a light microscope. Powder particle morphology and EDS analysis were performed on the SEM. The obtained results confirm that the preheating temperature of the substrate has a significant impact on structural mechanical properties of the tested coatings system.

**Keywords:** Atmospheric plasma spraying (APS), microstructure, interface, microhardness, bond strength  $ZrO_2$  8%  $Y_2O_3$ , Ni22Cr10Al1Y, microstructure, interface, microhardness, bond strength.

### 1. INTRODUCTION

Zirconia ( $ZrO_2$ ) based ceramic coatings, due to their specific properties, have found wide application for protection of parts that operate at high temperatures exposed to an oxidizing, hot corrosion and erosive surrounding environment. Depending on the application a large number of different dual coating systems are used, differing in chemical composition as well as the number of layers, their thickness, structure, porosity and method of obtaining [1-4]. Plasma spraying is one of the most common methods used for depositing multilayer coating systems [5]. Zirconium dioxide  $ZrO_2$  is used as the basic material for creating

thermal barriers and as a biomaterial for the manufacture of parts for hip implants in orthopedic surgery and crowns in dentistry. Using  $ZrO_2$  based ceramics as biomaterial is due to its good chemical and dimensional stability, mechanical strength, toughness and elastic modulus. In early development stages a few  $ZrO_2$ MgO,  $ZrO_2$ CaO i  $ZrO_2$ Y<sub>2</sub>O<sub>3</sub> solid solutions, which were used as thermal barriers, were tested for biomedical applications [6-8]. Currently in orthopedic surgery  $ZrO_2$  based ceramic implants are widely used. Deposits are formed from the flow of molten particles colliding with the base which are then deformed and rapidly cooled and solidified. Individual droplets flatten and spread creating thin lamellae that are further deposited onto the previous lamellae forming a deposit [5,6,8]. Thus in the deposit present are small voids, such as volume micro pores as volume faults with high concentrations of stress that cause the appearance of micro cracks. Limited binding of lamellae in the

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deposit decreases the values of microhardness, elastic moduli, fracture toughness and thermal conductivity of the corresponding material [9]. There have been several previous studies that analyzed the influence of preheating temperature of the substrate on the quality of inter-lamellar binding and the share of pores in the layers. Therefore, many studies have been conducted to understand the factors that determine the microstructure of the deposit, and in particular inter-lamellar binding within the deposit. Optimization of spray parameters has been done in order to modify the microstructure of the deposits [1,2,10-12]. Most research of the influence of substrate temperature was carried out at temperatures below 350°C, which are associated with the morphology of formed lamellae. To create a bond layer a MeCrAlY type alloy is used, where Me can be Co, Ni or Fe. The metal layer has to have a good bond with the substrate to enhance corrosion resistance and reduce the impact of residual stress in ceramics [1].

The NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> metal powder which is coated with Y<sub>2</sub>O<sub>3</sub> oxide is used as a stabilizer in ZrO<sub>2</sub> based ceramic coatings. The NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> was developed parallel with the ceramic powder ZrO<sub>2</sub>CeO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> [13,14]. The Y<sub>2</sub>O<sub>3</sub> oxide which is present in both powders improves the bond between the metal and ceramic layers. During the process of deposition the aluminum in the powder reacts with oxygen to form α-Al<sub>2</sub>O<sub>3</sub>. One part of the α-Al<sub>2</sub>O<sub>3</sub> reacts with Y<sub>2</sub>O<sub>3</sub> from the powder and forms ductile complex AlYO<sub>3</sub> and Al<sub>5</sub>YO<sub>3</sub> oxides of the dual Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> system [15]. As a result of a chemical reaction of the oxide the γ-Ni (Cr) solid solution lamellae were coated with this complex oxide which improves its cohesive strength. In the process of deposition an exothermic reaction also occurs with Al and Co which increases the adhesion of the bond coating to the substrate [13,15].

This study examined the NiCrAlCoY<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>CeO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> coating system. The powders were deposited using the atmospheric plasma spraying - APS process on cold and substrates preheated to a temperature of 180°C. The goal of substrate preheating was to improve inter-lamellar bond, microstructure and mechanical properties of the deposited layers. Metallographic tests were carried out to determine content of pores and oxides in the bond layers and micro pores in the ceramic coatings. Microhardness and tensile strength of the dual coating systems bond were also tested. Analyses of the test results made it possible to determine the influence of substrate preheating temperature on the structural mechanical properties.

## 2. EXPERIMENTAL PART

### 2.1. Materials and experimental details of plasma spray coatings deposition

The material onto which the coatings were deposited was made of stainless steel X15Cr13 (EN 1.4024) in thermally untreated condition. Powders of the Sulzer Metco company marked Metco 461 and Metco 205NS were used to create the dual coating systems [13,16]. The composite powder NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> that was used for the production of the bond coating is a NiCr alloy coated with 5.5wt%Al, 2.5wt%Co and 0.5wt%Y<sub>2</sub>O<sub>3</sub>. The NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> powder particles were produced by a coating method. Coating of NiCr cores was carried out with Al, Co and Y<sub>2</sub>O<sub>3</sub> particles from 1 to 10 microns in size using a suitable organic binder. Production of composite powder with the coating method enables exothermic reactions between the powder components during deposition. This thermal energy secures better binding of the coating to the substrate. The melting point of the powder is 1400°C, the coefficient of thermal conductivity 23-28 W/mK, and the coefficient of linear expansion  $13 \times 10^{-6}$  1/mK. Powder grain size is in the range of -150 + 45 μm [13]. The morphology of the NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> powder particles, which were used in the experiment, is shown in Figure 1. The powder particles are of irregular shape.

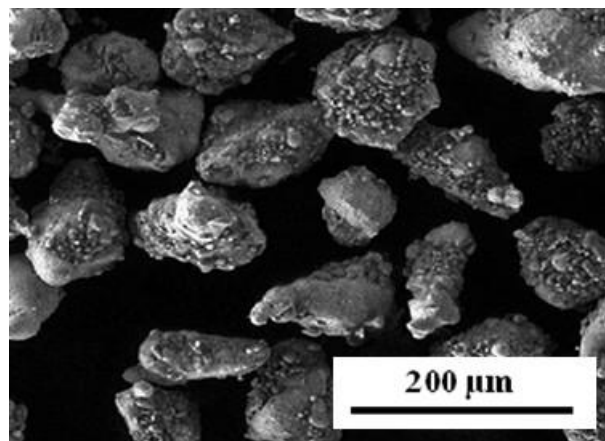


Figure 1. The morphology of NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> powder particles (SEM)

Slika 1. Morfologija čestica praha NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> (SEM)

The ceramic ZrO<sub>2</sub>CeO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub> powder is fully pre-alloyed with 24-26wt%CeO<sub>2</sub> and 2-3wt%Y<sub>2</sub>O<sub>3</sub>, the particles are made by homogenization in a furnace and a spheroidization process (HOSP). Typical impurities in the powder are Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> with less than 0.2wt%. The coefficient of thermal conductivity of the powder is very low 0.9 W/mK, the melting point is 2480°C, and the coefficient of

linear expansion is  $8.5 \times 10^{-6}/\text{mK}$  [16]. Powder grain size that was used in the experiment was in the range of  $-90 + 11\mu\text{m}$ . The morphology of the  $\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$  powder particles is shown in Figure 2. The SEM micrographs show that the powder particles are spherical in shape which allows their excellent flow in the plasma jet.

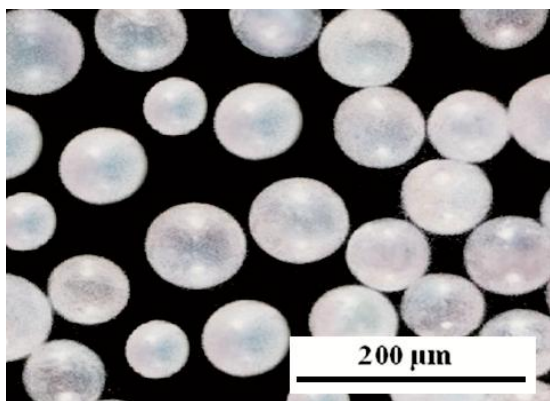


Figure 2. The morphology of  $\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$  powder particles (SEM)

Slika 2. Morfologija čestica praha  $\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$ (SEM)

The PlasmaDyn company atmospheric plasma spraying (APS) system and plasma spray gun SG - 100, with appropriate control spray conditions was used for deposition of the coatings system. Before depositing the coatings, the substrate surfaces were roughened with  $\text{Al}_2\text{O}_3$  white corundum using 0.7-1.5mm particles. As an arc gas and powder carrier gas Argon was used in combination with helium which was used as the plasma gas. The coatings were deposited with a power supply of 40KW. Detailed values of plasma spray parameters for the bond coat (BC) and the ceramic coatings (CC) are shown in Table 1.

Table 1. Powder deposition parameters

Tabela 1. Parametri depozicije praha

Deposition parameters	BC	CC
Plasma current, I (A)	950	950
Plasma voltage, U (V)	40	40
Primary plasma gas flow rate, Ar (l/min)	49	49
Secondary plasma gas flow rate, He (l/min)	35	35
Carrier gas flow rate, Ar (l/min)	6	8
Powder feed rate, (g/min)	45	45
Stand-off distance, (mm)	110	100

Analyses of structural and mechanical properties of the TBC were done according to ASTM C633-1 [17]. The base metal onto which the layers of coatings were deposited for microhardness testing and evaluation of microstructure in

deposited state is made of steel Č.4171 (X15Cr13 EN10027) containing 13% chromium in thermally untreated condition, 70x20x1.5mm in size. Base metals for testing bond strength were also made of the same steel  $\varnothing 25 \times 50$  mm in size.

Microhardness testing of layers was conducted using the  $\text{HV}_{0.1}$  method and tensile testing for the bond strength. Five readings of micro hardness values of layers were done, in the middle and at the ends of the samples of which the two extreme values were disregarded. Of the three remaining values the minimum and maximum values of microhardness of layers are shown to assess homogeneity. Testing of bond strength was performed at room temperature with a tension rate of 1cm/1 min. Five charges were tested, of which the two extreme values were disregarded. Of the three remaining values shown are the minimum and maximum values of bond strength. Powder particle morphology and EDS analysis of the TBC was performed by scanning electron microscopy (SEM). The microstructure of the deposited layers was examined on an optical microscope (OM). Analysis of the share of pores and oxides in the bond coating and oxides in the ceramic coatings was performed by examining 5 photos at 200x magnification. This paper presents the mean values of the share of micro pores and oxides in the bond coatings and micro pores in the ceramic coatings.

### 3. RESULTS AND DISCUSSION

#### 3.1. Results of coatings testing

The obtained values of microhardness of the coating systems, depending on the spray parameters used, are shown in Figure 3. Lower values of microhardness refer to the bond coatings and the larger values to the ceramic coatings. The microhardness values of the  $\text{NiCrAlCoY}_2\text{O}_3$  bond coating are directly related to the temperature of the substrate.

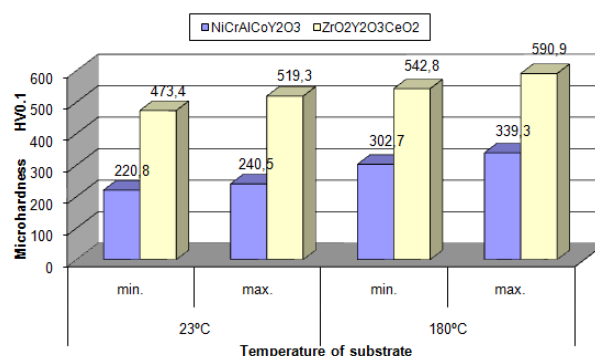


Figure 3. The values of micro hardness systems of  $\text{NiCrAlCoY}_2\text{O}_3/\text{CeO}_2\text{Y}_2\text{O}_3\text{ZrO}_2$

Slika 3. Vrednosti mikrotvrdoće sistema  $\text{NiCrAlCoY}_2\text{O}_3/\text{CeO}_2\text{Y}_2\text{O}_3\text{ZrO}_2$

The average value of microhardness of bond layers deposited on cold substrates is  $230,6HV_{0,1}$  and for layers deposited on preheated substrates it was  $321HV_{0,1}$ . The layers deposited on the preheated substrates have higher values for an average of  $90,3HV_{0,1}$ , indicating that the microhardness of the coatings increases with increasing temperature of the substrate. Incompletely deformed molten droplets and unmelted particles on cold substrates make a structure which shows greater porosity than those in deposits formed on the preheated substrate. Heating of the substrate resulted in the formation of coatings with good binding of lamellae at the substrate interface and through the coating layers. Better inter-lamellar contact contributed to obtaining denser layers with a smaller share of the pores, as confirmed by metallographic examination.

The microhardness values of  $ZrO_2CeO_2Y_2O_3$  ceramic layers were also higher on preheated substrates. The average value of microhardness of ceramic layers deposited on cold substrates was  $496,3HV_{0,1}$  and of the layers deposited on preheated substrates it was  $566,8HV_{0,1}$ . The layers deposited on preheated substrates on average had higher values of microhardness of  $70,5HV_{0,1}$ . Higher values of microhardness of ceramic layers deposited on preheated substrates indicate greater cohesive strength between the lamellae, which is confirmed by the results of tensile strength. Substrate preheating resulted in the increase of contact temperature between the molten ceramic particles and in the values of microhardness of the coatings. Interfacial lamellar binding is directly dependent on the substrate temperature. Accordingly, higher values of microhardness are associated with improved inter-lamellar binding through the layers and increased adhesion of the coating, which the bond strength tests have confirmed. The tensile strength was high for the  $NiCrAlCoY_2O_3/ZrO_2CeO_2Y_2O_3$  coatings systems, Figure 4. Layers deposited on the preheated substrate formed coatings with higher tensile strength.

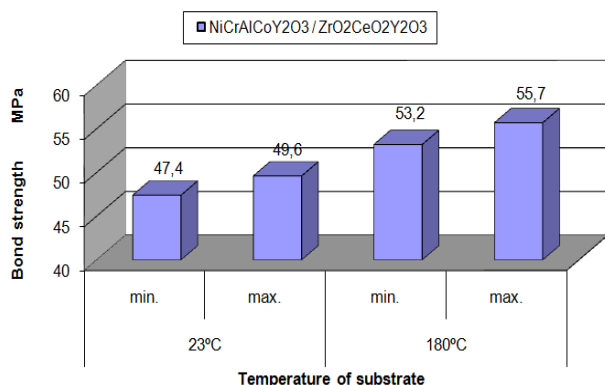


Figure 4. The values of bond strength TBC systems

Slika 4. Vrednosti čvrstoće spoja TBC sistema

For all coatings systems high values of tensile bond strength were obtained due to  $Y_2O_3$  oxide which was also present in the bond and the ceramic coatings. This type of oxide influenced better inter-lamellar cohesive strength between the bond and the ceramic layer.

The maximum value of bond strength of  $55,7MPa$  was obtained from the coating system deposited on a preheated substrate; while the lowest value of  $47,4MPa$  was obtained from the coating system deposited on a cold substrate. Measured values indicate that the substrate temperature affects the tensile strength of the coatings systems. Preheating the substrate resulted in increase of coatings adhesion and improvement of the microstructure. The fracture mechanism of the TBC system deposited on preheated substrate was adhesive at the substrate/bond coating interface. On cold substrates the fracture mechanism took place largely at the bond coating/ceramic coating interface, and to a lesser extent at the substrate/bond coating interface.

Quantitative analysis of the total content of pores and oxides in bond coatings and the total content of the pores in the ceramic coatings showed that the measured values were directly linked to the temperature of the substrate, Figure 5. In the bond coatings deposited on cold substrates the total content of pores and oxides was  $22,7\%$ , and in coatings deposited on preheated substrates it was  $19,5\%$ . The measured values were below  $28\%$  which were indicated by the powder manufacturer[13]. In the ceramic coatings deposited on preheated substrates the content of pores was  $15,5\%$ , and in coatings deposited on cold substrates it was  $18,2\%$ . The measured values of the content of pores and oxides in the bond layers and the content of the pores in the ceramic layers were in accordance with microhardness and microstructures.

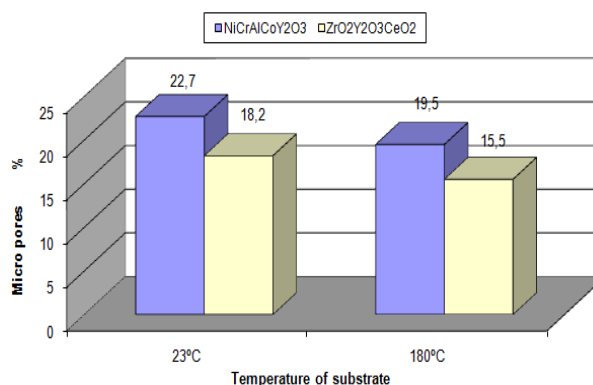


Figure 5. The values of pore content in TBC systems

Slika 5 Vrednosti sadržaja pora u TBC sistemima



Microstructures of  $\text{NiCrAlCoY}_2\text{O}_3$  layers deposited on preheated and cold substrates are shown in Figure 6.

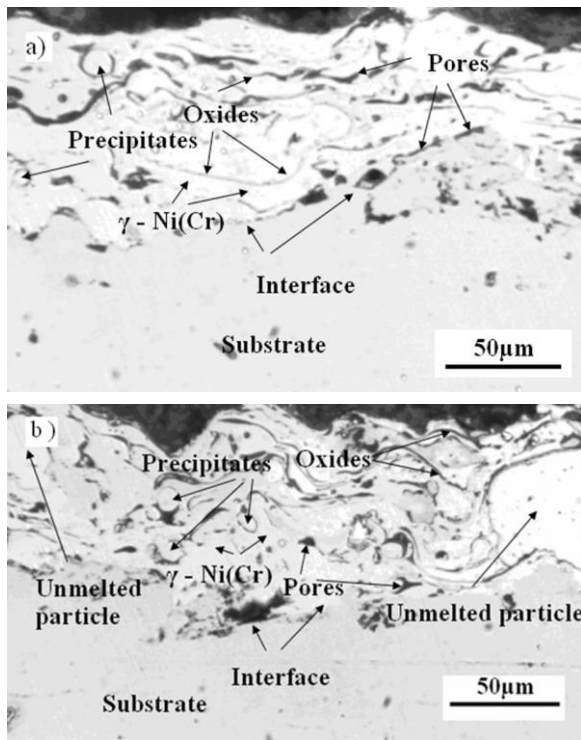


Figure 6. Microstructure  $\text{NiCrAlCoY}_2\text{O}_3$  (a) sample preheated and (b) sample cold

Slika 6. Mikrostruktura  $\text{NiCrAlCoY}_2\text{O}_3$  (a) predgrejan uzorak i (b) hladan uzorak

The bond coatings showed a uniform lamellar structure. Boundaries at the interface between the substrate and  $\text{NiCrAlCoY}_2\text{O}_3$  coating can be clearly seen. At the substrate/ceramic layer interface there are no microcracks and macrocracks and there is no separation of coating layers or flaking off the metal substrates. The microstructure of layers deposited on preheated substrate is uniform throughout the cross-section of the deposit which shows improved inter-lamellar contact. There are no unmelted particles in the structure, while a smaller proportion of precipitates are present. The base of the  $\text{NiCrAlCoY}_2\text{O}_3$  coating consists of a light white colored solid solution of chromium in nickel  $\gamma$ -Ni(Cr). Through the  $\text{NiCrAlCoY}_2\text{O}_3$  layers, inter-lamellar  $\alpha$ - $\text{Al}_2\text{O}_3$  oxides and complex  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  dual system oxides, which are evenly distributed in the coatings, can clearly be seen. Longitudinal  $\alpha$ - $\text{Al}_2\text{O}_3$  oxide lamellae and complex  $\text{AlYO}_3$  and  $\text{Al}_5\text{YO}_3$  oxides of the  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  dual system are formed in a liquid state in the plasma [9]. Lamellae of the  $\gamma$ -Ni(Cr) solid solution are coated with these oxides. Irregularly shaped micropores are present in the structure and marked with black arrows. Through bond coating layers deposited on a cold substrate observed clearly are

unmelted particles and micro pores with a higher share of precipitates. In the  $\text{NiCrAlCoY}_2\text{O}_3$  coating structure there are no micro or macrocracks observed. Figure 7 (a and b) shows microstructures of  $\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$  ceramic coatings. Pre-heating of the substrate had significant influence on the content of the micro pores in the ceramic layers. Deformation of molten ceramic droplets on impact with the substrate at local level in the coating plays an important role in determining defects such as porosity, microstructure, microhardness, cohesive strength and adhesion. Layers deposited on preheated substrates exhibit lower porosity due to more uniform deformation of molten droplets on impact with the substrate. Improved contact between the deposited particles and lower porosity lead to an increase in thermal conductivity of the ceramic coating. In the ceramic layers visible are larger dark surfaces created by pulling out fragments of ceramics from the base of the coating during sample preparation (pull-outs). Due to good inter-lamellar bond in ceramic layers deposited on the preheated substrates, this effect is much less pronounced compared to ceramic layers deposited on cold substrates. The microstructure of coatings deposited on cold substrates show a typical structure with limited inter-lamellar bonding.

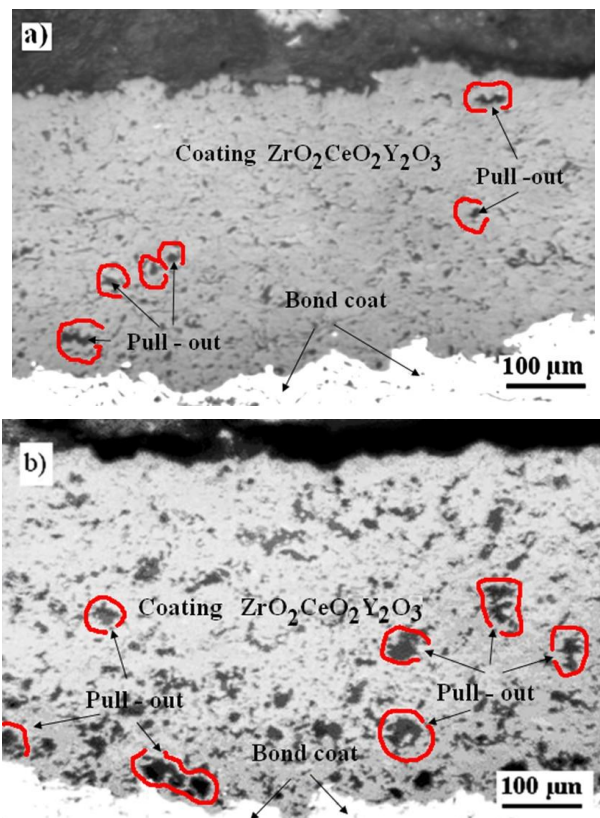


Figure 7 Microstructure  $\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$  (a) sample preheated and (b) sample cold

Slika 7. Mikrostruktura  $\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$  (a) predgrejanuzoraki (b) hladanuzorak

Limited inter-lamellar bonding made it easier to pull out larger portions of ceramic particles from the coating base. Black fields (pull outs) can clearly be seen in the structure, circled in red. These fields were not taken into account in establishing the total content of micropores in the ceramic coatings. Porosity is obviously higher in the ceramic coating deposited on a cold substrate. Low temperature of the substrate obviously limited plastic deformation of the ceramic particles on impact with the base and thus reduced the inter-surface bonding of the lamellae through the deposited layers, which caused a higher porosity in the coating. Due to higher pore content the layers have lower density and lower microhardness, which is consistent with the measured values, Figure 5.

Accordingly, higher values of microhardness of ceramic layers on preheated substrates are associated with improved inter-lamellar bonding. Content of pores is very important in the ceramic layers. Insulating properties of TBC are directly related to the shares of pores. The layers with smaller pore content have higher heat conductivity and less insulating properties. Figure 8 shows (SEM) Microstructure of TBC system deposited on a preheated substrate. In the microstructure of deposited  $\text{NiCrAlCoY}_2\text{O}_3$  coatings there are obvious changes in the stoichiometric ratio of elements in comparison with the composition of the composite  $\text{Ni}_{17.5}\text{Cr}_{-5.5}\text{Al}_{-2.5}\text{Co}_{-0.5}\text{Y}_2\text{O}_3$  powder. Based on performed measuring and the EDS results shown in Figure 9 and Table 2 stoichiometric changes within the marked region (ED2) are expected.

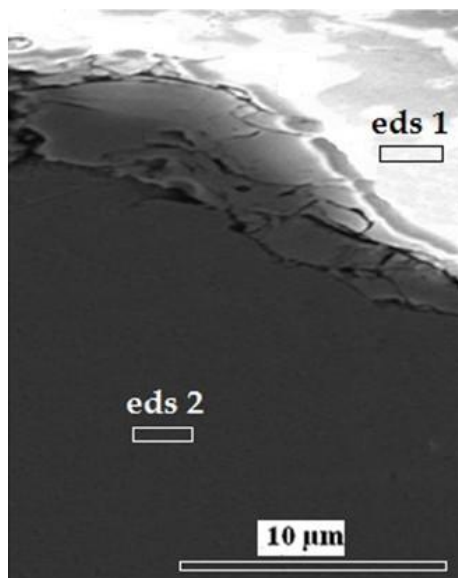
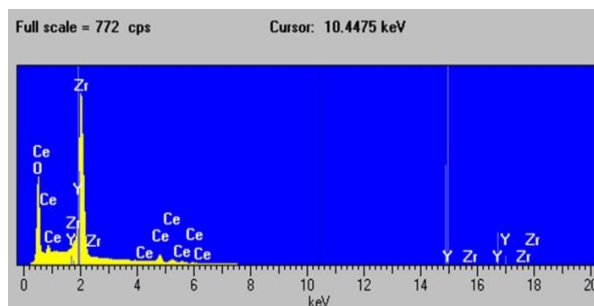
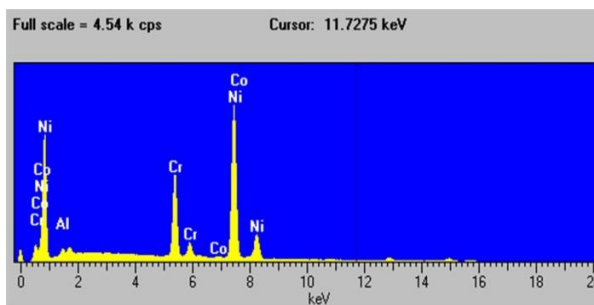


Figure 8. SEM microphotography of TBC -  $\text{NiCrCoAlY}_2\text{O}_3/\text{ZrO}_2 \text{ CeO}_2 \text{ Y}_2\text{O}_3$

Slika 8. SEM mikrografija TBC -  $\text{NiCrCoAlY}_2\text{O}_3/\text{ZrO}_2 \text{ CeO}_2 \text{ Y}_2\text{O}_3$



a) eds1



b) eds2

Figure 9. EDS  $\text{ZrO}_2 \text{ CeO}_2 \text{ Y}_2\text{O}_3 / \text{NiCrCoAlY}_2\text{O}_3$  in figure 8 (a) eds1i (b) eds2

Slika 9. EDS  $\text{ZrO}_2 \text{ CeO}_2 \text{ Y}_2\text{O}_3 / \text{NiCrCoAlY}_2\text{O}_3$  na slici 8 (a) eds1i (b) eds2

Table 2. Powder deposition parameters

Tabela 2. Parametri depozicije praha

%	eds 1	%	eds2
O	66.52	O	-
Zr	24.68	Al	0.92
Ce	8.00	Cr	18.94
Y	0.8	Co	3.32
Ni	-	-	76.82

In the  $\text{NiCrCoAlY}_2\text{O}_3$  coating there has been a change in the stoichiometric elements Al, Co and Cr caused by the reaction of Al with oxygen and the exothermic reaction of Al and Co. Due to the exothermic reaction of Al with Co during the deposition of the powder, the  $\text{NiCrCoAlY}_2\text{O}_3/\text{ZrO}_2 \text{ CeO}_2 \text{ Y}_2\text{O}_3$  coating system showed high value of the bond strength. In the process of depositing the Al reacted with oxygen in an extremely high share, forming  $\alpha\text{-Al}_2\text{O}_3$  oxide and complex dual system  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$  oxides. In the solid  $\gamma$  -  $\text{Ni}(\text{Cr})$  solution Al is present with an extremely small share of 0.92%, which was confirmed by (eds 2) analysis. Figure 9 a) shows the deposited  $\text{ZrO}_2 \text{ Y}_2\text{O}_3 \text{ CeO}_2$  coating on the bond coating, analysis (eds 1).

#### 4. CONCLUSIONS

Testing of the  $\text{NiCrAlCoY}_2\text{O}_3/\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$  layers coating showed the influence of preheating temperature of the substrate on the mechanical properties and microstructure.

The microhardness values of the bond coatings and ceramic coatings are directly related to the temperature of the substrate. The layers deposited on the preheated substrates had higher values of microhardness than the layers deposited on cold substrates. Heating of the substrate enabled forming of thicker coatings with better inter-lamellar contact.

The bond tensile strength indicates that the substrate temperature has significant influence on the connection between the substrate and the deposited coating system. Pre-heating of the substrate influenced increased adhesion of the coating. The greatest values of joint strength had the coating systems deposited on preheated substrates.  $\text{Y}_2\text{O}_3$  oxide simultaneously present in both powders additionally influenced better inter-lamellar cohesive strength between these two layers.

Quantitative analysis of the total content of pores and oxides in bond coatings and the total content of the pores in the ceramic coatings showed that these values are in direct relation to the temperature of the substrate. Pore content was lower in coatings deposited on a preheated substrate. The values of the content of pores and oxides in the coatings were in accordance with the microhardness and microstructure.

Microstructures of bond coatings had a uniform lamellar structure. At the interface with the substrates and ceramic layers there were no micro or macro cracks present and there was no spalling off or flaking of the coating system from the substrate. The layers deposited on the preheated substrates were denser. In the layers deposited on the preheated substrates there were no unmelted particles present, while in the layers deposited on a cold substrate unmelted particles were found. In the microstructure of the bond coating there was a change of the stoichiometric ratio of elements in comparison with the composition of the composite powder. The Al reacted with oxygen in high proportion, forming  $\alpha\text{-Al}_2\text{O}_3$  oxide and complex  $\text{AlYO}_3$  and  $\text{Al}_5\text{YO}_3$  oxides of the  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$  dual system. In the  $\gamma\text{-Ni}$  (Cr) solid solution Al is present with an extremely small share of 0.92%.

Ceramic layers showed a porous microstructure with different shares of pores depending on the temperature of the substrate. The minimum content of pores was measured in the ceramic coatings deposited on a preheated substrate, which showed the best structural and

mechanical properties of the coatings system. Based on results presented the conclusion can be that the pre-heating of the substrate can significantly affect the mechanical properties and microstructure of the  $\text{NiCrAlCoY}_2\text{O}_3/\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$  coatings system.

#### Acknowledgement

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#### 5. REFERENCE

- [1] M.R.Mrdak, A.Vencl, B.D.Nedeljkovic, M.Stanković (2013) Influence of plasma spraying parameters on properties of the thermal barrier coatings, *Materials Science and Technology*, 29(5), 559-567.
- [2] M.Mrdak, M.Rakin, B.Medjo, N.Bajić (2015) Experimental study of insulating properties and behaviour of thermal barrier coating systems in thermo cyclic conditions, *Materials & Design*, 67, 337-343.
- [3] W.Gong, R.Li, Y.Li, D.Sun, W.Wang (2013) Stabilization and corrosion resistance under high-temperature of nanostructured  $\text{CeO}_2/\text{ZrO}_2\text{-Y}_2\text{O}_3$  thermal barrier coating, *Acta Metallurgica Sinica*, 49, 593-598.
- [4] A.Thibblin, S.Jonsson, U.Olofsson (2018) Influence of microstructure on thermal cycling lifetime and thermal insulation properties of yttria-stabilized zirconia thermal barrier coatings for diesel engine applications. *Surface Coatings Technology*, 350, 1-11.
- [5] M.R.Mrdak (2016) *Plazma sprej procesi i svojstva zaštitnih prevlaka*, knjiga, Beograd, Srbija.
- [6] M.R.Mrdak (2021) *Savremene višenamenske plazma sprej prevlake*, monografija, Beograd, Srbija.
- [7] J.M.Drouin, B.Cales, J.Chevalier, G.Fantozzi (1997) Fatigue behavior of zirconia hip joint heads: experimental results and finite element analysis, *Journal of Biomedical Materials Research*, 34, 149-155.
- [8] M.Mrdak, Č.Lačnjevac, M.Rakin, D.Veljić, D.Bajić (2021) Characterisation of biocompatible layers of  $\text{ZrO}_2\text{8%Y}_2\text{O}$  used in combination with other ceramics to modify the surface of implants, *Zastita materijala*, 62(4), 262 - 268.
- [9] M.Mrdak (2003) Uticaj parametara plazma depozicije na kvalitet termalnih barijera sa povišenom otpornošću na termociklični zamor, *Doktorska disertacija*, Novi Sad.
- [10] A.Vencl, S.Arostegui, G.Favaro, F.Zivic, M.Mrdak, S.Mitrović, V.Popovic (2011) Evaluation of adhesion/cohesion bond strength of the thick plasma spray coatings by scratch testing on

- coatings cross-sections, Tribology International, 44(11),1281-1288.
- [11] M.Mrdak (2017) Mechanical properties and the microstructure of the plasma-sprayed  $ZrO_2Y_2O_3/ZrO_2Y_2O_3CoNiCrAlY/CoNiCrAlY$  coating, Vojnotehnički glasnik / Military Technical Courier, 65(1), 30-44.
- [12] M.Mrdak, Č.Lačnjevac, M.Rakin, N.Bajić D.Veljić (2019) Karakterizacija plazma sprej bioinertne prevlake  $Al_2O_328tež.\%MgO$ , Zastita materijala, 60(1), 44-49..
- [13] MaterialProductDataSheet (2014) Metco 461NS, NickelChromiumAluminumCobaltYttria Composite Powder, DSMTS-0096.2 – NiCrAlCoYO Composite Powder, Oerlikon Metco.
- [14] M.Mrdak, Č.Lačnjevac, M.Rakin, D.Veljić, D.Bajić (2021) Characterization of deposited plasma spray NiCrAlCoY<sub>2</sub>O<sub>3</sub> coating layers on AlMg1 alloy substrates, Zastita materijala, 62(1), 34 – 40.
- [15] A.Vencl, M.Mrdak (2019) Thermal cycling behaviour of plasma sprayed NiCr-Al-Co-Y<sub>2</sub>O<sub>3</sub> bond coat in thermal barrier coating system, Thermal Science, 23(6B), 3985-3992.
- [16] MaterialProductDataSheet (2014) Metco 205NS, Ceria-Yttria Stabilized Zirconium Oxide HOSP Powder, DSMTS-0038.1 – CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> HOSP Powder, Oerlikon Metco.
- [17] ASTM C633-1 (2008) Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings, Reapproved.

## IZVOD

### KARAKTERIZACIJA PREVLAKE CIRKONIJUM OKSIDA STABILIZOVANOG CERIJUM I ITRIJUM OKSIDOM DEPONOVANE NA VEZNOJ PREVLAČI NIKL HROM ALUMINIJUM KOBALT ITRIJUM OKSID

Cirkonijum dioksid  $ZrO_2$  se koristi kao osnovni materijal za izradu termalnih barijera i kao biomaterijal za izradu delova implanata kuka u ortopedskoj hirurgiji i u stomatologiji za izradu kruna. Korišćenje  $ZrO_2$  keramičke kao izolacionog i biomaterijala je njena dobra hemijska i dimenzionalna stabilnost, mehanička čvrstoća, žilavost i modul elastičnosti. Cilj rada bio je da se analiziraju karakteristike prevlake cirkonijum oksida stabilizovanog cerijum i itrijum oksidom deponovane plazma sprej (APS) postupkom na veznoj prevlaci nikl hrom aluminijum kobalt itrijum oksid. Prevlake su deponovane na hladnim substratima i na predgrejanim substratima na temperaturi 180 °C. Za izradu veznih slojeva primenjen je kompozitni prah nikl hrom/aluminijum/kobalt/itrijum oksid, a za izradu keramičkih slojeva prah cirkonijum oksida stabilizovanog cerijum i itrijum oksidom. Ispitivanje kvaliteta prevlaka je urađeno merenjem mikrotvrdoće slojeva metodom HVi zatezne čvrstoće spoja sistema prevlaka ispitivanjem na zatezanje. Metalografska procena udela pora u veznim i keramičkim slojevima je urađena image analizom - obradom slika sa svetlosnog mikroskopa. Morfologije čestica prahova i EDS analiza je urađena na SEM-u. Dobijeni rezultati potvrđuju da temperatura predgrevanja substrata ima bitan uticaj na strukturno mehanička svojstva testiranih sistema prevlaka.

**Ključne reči:** Atmosferski plazma sprej (APS), mikrostrukture, interfejs, mikrotvrdoće, čvrstoća spoja.

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