



Vojnotehnicki glasnik/Military Technical
Courier

ISSN: 0042-8469

vojnotehnicki.glasnik@mod.gov.rs

University of Defence
Serbia

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CHROMIUM - ALUMINUM - YTTRIUM COATINGS

Vojnotehnicki glasnik/Military Technical Courier, vol. 61, núm. 4, 2013, pp. 26-47

University of Defence

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CHARACTERIZATION OF VACUUM PLASMA SPRAYED COBALT - NICKEL - CHROMIUM - ALUMINUM - YTTRIUM COATINGS

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DOI: 10.5937/vojtehg61-2495

FIELD: Chemical Technology

ARTICLE TYPE: Original Scientific Paper

Summary:

This paper analyzes the influence of the plasma spray distance on the microstructure and the mechanical properties of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coatings deposited with the vacuum plasma spraying (VPS) procedure. The microstructure and the mechanical properties of the plasma spray coatings were determined by the interaction of the Ar/H₂ plasma ions with the powder particles when the transfer of the speed and temperature of ions on the powder particles occurs. The effect of interaction directly depends on the time of the interaction between ions and powder particles, which is defined by the plasma spraying distance. The powder is deposited by the plasma gun F4 at three substrate distances: 270, 295 and 320 mm. The coating with the best structural and mechanical properties was tested on the oxidation in a furnace for heat treatment without protective atmosphere at 1100°C in a period of 240 hours. The morphology of the powder particles was examined on the SEM. The microstructure of the layers in the deposited condition was tested by light microscopy. The coating with the best mechanical properties was electrolytically etched with 10% oxalic acid solution H₂C₂O₄·2H₂O. The analysis of the microstructure of the etched coating was performed by light microscopy and on the SEM, before and after testing the coating on oxidation. The microstructural analysis of the deposited layers was performed in accordance with the 'Pratt-Whitney' standard. The mechanical properties of the layers were assessed through the examination of microhardness by the HV_{0.3} method and through bond strength tensile testing.

Key words: yttrium; vacuum; powders; plasmas; particles; microstructures; mechanize; mechanical properties; deposits; coatings.

* ACKNOWLEDGEMENT: The author is thankful for the financial support from the Ministry of Education and Science of the Republic of Serbia (national projects OI 174004, TR 34016).

Introduction

Systems of CoNiCrAlY coatings have been developed based on the systems of NiCrAl, FeCrAlY, NiCrAlY and CoCrAlY coatings (Mrdak, 2010, pp.5-16), (Mrdak, 2012, pp.182-201), (Driver, 2004), (Feuerstein, et al., 2008, pp.199-213). The CoNiCrAlY coatings are used in different applications for the protection of gas turbines against high temperature oxidation and hot corrosion. Since the properties and the behavior of coatings are closely related to the microstructure, it is necessary to examine the structure of coatings after deposition and oxidation at elevated temperatures (Gudmundsson, Jacobson, 1988, pp.207-217). In order to understand the performance of Co-based CoNiCrAlY coatings better, it is necessary to understand the role of each element in the coating. With the increase of the Al content, its effect in the coating increases. The Al content should be high enough to form and maintain the α - Al_2O_3 oxide layer which prevents subsequent oxidation (Prescott, Graham, 1992, pp.233-254). For this type of coatings, a typical content of Al is 10 -12 wt%. Aluminum in CoNiCrAlY alloys, forms the β (Co, Ni) Al phase which serves as a reservoir for the renewal of the protective α - Al_2O_3 oxide. Co-based alloys with Al produce the β - CoAl phase which improves the resistance of these alloys to sulphidation, they also produce the β - NiAl phase which improves the resistance of these alloys to high temperature oxidation. It is also certain that the addition of Nickel to a Co-Cr-Al alloy reduces the process of interaction between the coating and the superalloy (Tamarin, 2002). The presence of Y improves the bonding of the α - Al_2O_3 oxide with the coating (Bose, 2007), (Brandl, Tamarin, et al., 1998, pp.10-15). Peng et al. found that the presence of Y prevents the forming of cavities at the interface with the substrate (Peng, et al., 2003, pp.2293-2306). Moreover, the Y content is of crucial importance for the growth of the TGO oxide on the coating surface (Toscano, et al., 2006, pp.3906-3910). A high content of Y leads to a high rate of the TGO growth, which is unfavorable and harmful for the coating.

CoNiCrAlY coatings are often deposited by the plasma spraying process in the vacuum (VPS). The development of the VPS technology has led to a significant improvement of the quality in coatings in comparison with the coatings produced at the atmospheric pressure. The main difference is that the process is performed in the vacuum in the absence of air at low pressure under the conditions of a high level of cleanliness and with the use of the transferred arc for cleaning the surface of the substrate. In its deposited condition, the microstructure of the CoNiCrAlY coating consists of two phases, γ and β . The γ phase is a solid solution of Co, Ni and Cr. The β (Co, Ni) Al phase is formed from

the β - CoAl phase and the β - NiAl phase. The present β phase and its share in the structure are essential for the protection of CoNiCrAlY coatings. The service life of the CoNiCrAlY coating in oxidation conditions is directly related to the amount of the β -phase which occurs in a variety of morphologies associated with different degrees of cooling related to different sizes of powder particles during spraying (Poza, Grant, 2006, pp.2887-2896). The elongated morphology of the β phase within γ grains and small β grains located on the border between the γ grains were associated with rapid cooling of melted small powder particles. Larger β grains were associated with larger particles and slower cooling (Poza, Grant, 2006, pp.2887-2896). In the Co-based CoNiCrAlY alloy there is no γ' phase present (Tamarin, 2002). The reason for the absence of the γ' phase in this alloy has been explained by some researchers (Achar, et al., 2004, pp.272-283), (Czech, et al., 1995, pp.28-33), who claim that Co tends to decrease the γ' phase. The stability of the β (Co, Ni) Al phase is reduced at high temperatures due to the diffusion of Al. Cheruvu and Mobarra with associates (Cheruvu, et al., 2000, pp.50 - 54), (Mobarra, et al., 2006, pp. 2202-2207) have found that, at high temperatures, Al from the β phase fills the oxide layer on the coating surface and takes Al out of the β phase. By exposing the CoNiCrAlY alloy to 1100°C the TGO zone with a protective α - Al_2O_3 oxide layer is formed on the surface. In the zone near the protective α - Al_2O_3 oxide layer, there is no β -(Ni, Co) Al phase because the surface layer is Al depleted (Nicholls, Bennett, 2000, pp.413-428). Only a small amount of Al remains in the regions rich in (Ni, Co) (Leea, 2005, pp.239 - 242). In this area, there is the Al-depleted β - zone which is below the upper TGO oxide layer. The thickness of the depleted β - zone increases with a longer exposure of the alloy to high temperatures due to aluminum consumption and the growth of the TGO layer (Nicholls, Bennett, 2000, pp.413-428). During the oxidation, protective oxide cracks and peels off from the surface and the aluminum from inner coating layers diffuses to the surface and restores a protective surface oxide layer (Nicholls, Bennett, 2000, pp.413 - 428), (Wang, et al., 2002, pp.70 - 75), (Gurrappa, Sambasiva, 2006, pp.3016-3029). In the TGO zone, besides the α - Al_2O_3 oxide, there are spinel compounds such as CoAl_2O_3 and NiAl_2O_3 or (Ni, Co)(Al, Cr) $_2\text{O}_4$ (Tang, et al., 2004, pp.228-233). Aluminum depletion near the surface leads to the transformation of the β (Ni, Co) Al phase into the γ' - Ni_3Al phase. The extending of oxidation causes the growth of this area and the transformation of the γ' - Ni_3Al phase into the γ -solid solution. As a result, the coating degrades (Jiang, et al., 2010, pp.2316-2322), (Mobarra, et al., 2006, pp.2202-2207). The oxidation of the γ phase in the depleted β - zone occurs with a faster formation of a protective oxide shell. CoNiCrAlY coatings in the deposited condition

have a high bond strength of 55 - 62MPa and micro hardness of 558 ± 43 HV_{0.3} for the average value of porosity of 4.2% (Material Product Data Sheet, 2011, DSMTS–0092.1, Sulzer Metco). In addition to good mechanical properties, the coatings have a low coefficient of friction of 0.85 - 0.9 and are resistant to wear (Gudmundsson, Jacobso, 1988, pp.207-217). The recommendation of the powder manufacturer for the CoNiCrAlY coating operating temperature is $\leq 1050^{\circ}\text{C}$ (Material Product Data Sheet, 2011, DSMTS–0092.1, Sulzer Metco).

The paper presents the results of experimental investigations of the impact of spray distances at low pressure on the mechanical properties and the microstructure of Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating layers. Three groups of samples were made with three different distances of plasma guns: 270, 295 and 320mm. The coating with the best properties was tested on oxidation in a heat treatment furnace without protective atmosphere at 1100°C for a period of 240 hours. The main aim of this study was to make Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating layers homologous and to apply them on aeronautical parts exposed to a combination of high temperature oxidation and hot corrosion. The microstructure and mechanical properties of the coating layers were analyzed and the coating with the best quality was selected.

Materials for testing and samples

The powder produced by the 'Sulzer Metco' (Sulzer Metco) company, marked AMDRY 9951, was used for the experiment. The Co₃₂Ni₂₁Cr₈Al_{0.5}Y powder was developed for the production of coatings used to protect the base metal from high temperature oxidation and hot corrosion at temperatures $T \leq 1050^{\circ}\text{C}$ (Material Product Data Sheet, 2011, DSMTS-0092.1, Sulzer Metco). The metal powder was produced by the atomization of liquid melted Co₃₂Ni₂₁Cr₈Al_{0.5}Y alloy with the inert gas of Argon. The produced particles of a spherical shape have a good flow in the jet plasma. Figure 1 shows the scanning electron microphotography (SEM) of the morphology of Co₃₂Ni₂₁Cr₈Al_{0.5}Y powder particles. The range of the granulation of powder particles used in the experiment was from 5 to 37 μm .

The basis for deposited coatings for testing microhardness and evaluating the microstructure in the deposited condition was made of Č.4171 (X15Cr13 EN10027) steel in thermally unprocessed condition with the dimensions: 70x20x1.5mm (Turbojet Engine - Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). The samples for testing the coating microstructure on oxidation at 1100°C were made of alloy NIMONIC 80A with the dimensions: 70x20x1.5mm (Turbojet Engine - Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

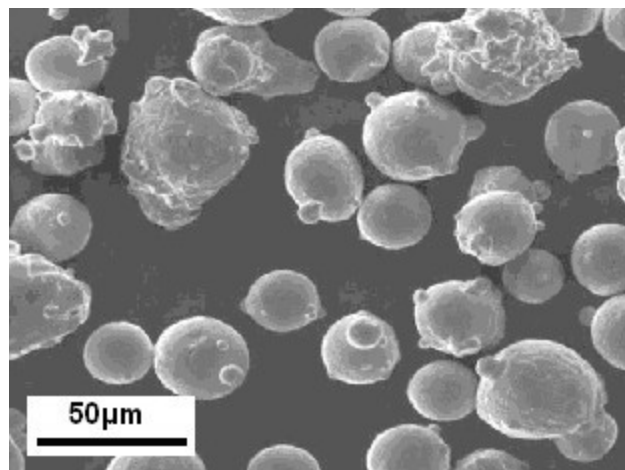


Figure 1 – (SEM) Scanning electron micrography of Co₃₂Ni₂₁Cr₈Al_{0.5}Y powder particles
 Slika 1 – (SEM) Skenirana elektronska mikrofografija čestica praha Co₃₂Ni₂₁Cr₈Al_{0.5}Y

The substrate for testing the bond strength was also made of Č.4171 (X15Cr13EN10027) steel in thermally unprocessed condition with the dimensions: Ø25x50 mm (Turbojet Engine - Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

Examination of microhardness, bond strength, and microstructure

The evaluation of the mechanical properties of layers was done by examining the layer microhardness with the HV_{0.3} method and by examining the bond strength by tensile testing. The microhardness was measured along lamellae, in the middle and at the ends of the samples. Five readings were performed and their values averaged.

The method of testing bond strength is the tensile testing method. The testing was done at room temperature with a tensile speed of 1cm/60s. Three test tubes were tested for each group of samples.

The morphology of powder particles was examined by the SEM method. The microstructure of layers in the deposited condition, after etching, was examined by light microscopy. The coating with the best mechanical properties, thermally treated to the oxidation at 1100°C for a period of 240 hours, was tested with a scanning electron microscope (SEM). The etching of the coating was done electrolytically with 10% of oxalic acid - H₂C₂O₄·2H₂O.

Powder deposition

The powder was deposited at low pressure in the vacuum with a mixture of plasma gases Ar-H₂. Figure 2 shows the vacuum plasma spray (VPS) system by the company 'Plasma Technik AG', designed for the protection of aeronautical parts exposed to a combination of excessive oxidation and hot corrosion. In the vacuum chamber there is a rotary table, a planetary system with 48 tools, a six-axis robot and an artificial arm. The handling system is designed in such a way that the tool and the substrates simultaneously rotate around their axes. Such complex movement allows even cleaning with the transferred arc and depositing powder evenly on the entire surface of the substrate. Table 1 shows the VPS parameters of the deposition of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y powder on the samples. The deposition of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating on the substrates of the samples was performed in the following way. The substrates were mounted into the supporting tools that were on the planetary system rotating around its axis. After the substrate mounting, the vacuum chamber was closed. The entire system is automated and programmed on the robot microprocessor unit. All parameters are given in the program. The process of vacuuming the chamber, the flow of plasma gas, cleaning of the substrate, the flow of powder, the deposition, the cooling of the substrate and the ventilation of the vacuum chamber are completely time-synchronized.

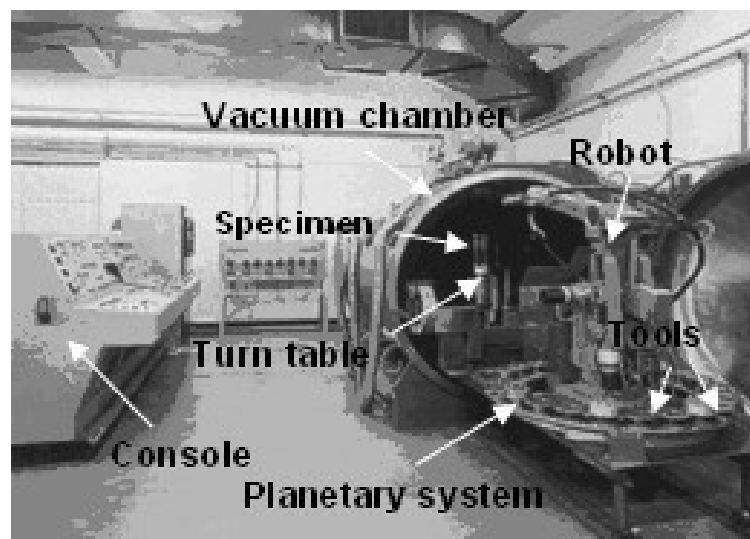


Figure 2 – Vacuum plasma spray system
Slika 2 – Vakuum plazma sprej sistem

Table 1 – Plasma spray parameters
Tabela 1 – Plazma sprej parametri

Parameters	Values	
	Cleaning arc	Spraying
Plasma current, I (A)	500	700
Plasma Voltage, U (V)	65	60
Primary plasma gas flow rate Ar (l/min)	50	50
Secondary plasma gas flow rate He ⁽¹⁾ , H ₂ ⁽²⁾ (l/min)	10 ⁽¹⁾	9 ⁽²⁾
Carrier gas flow rate (l/min)	--	3
Powder feed rate (g/min)	--	40
Stand-off distance (mm)	270	270 / 295 / 320
Chamber pressure (mbar)	25	120
Nozzle diameter (mm)	8	8
Speed of the gun (mm /s)	15	15

In the sealed chamber, the artificial hand that accepts the tool with the substrate from the planetary system and sets it on the rotary table is on the other side of the chamber opening and cannot be seen in Figure 2. After the mounting of the tool with the substrate, the chamber was vacuumised and a pressure of 10^{-3} mbar was reached in 5 minutes. Ar was then injected into the vacuum chamber through the plasma gun anode to the level of pressure of 25 mbar. At this pressure, all surfaces of the substrate were cleaned using the transferred arc. The distance of the plasma guns from the the surface of all the substrates was 270 mm. The plasma gun was set on (+) pole, and the substrate on (-) pole. This relation, called direct polarity, allows the oriented ions of the secondary gas He to clean the substrate surface from the impurities with a high speed and energy, making the substrate surface reactive. After the substrate cleaning, the powder was deposited on the substrates. The secondary plasma gas H₂ was added to the primary gas Ar. The pressure in the chamber was increased to the level of the operating pressure of 120 mbar. The constant pressure during deposition is provided by the vacuum pump. When the working pressure of 120 mbar was reached, the powder was injected into the plasma gun. The deposition rate is constant and does not change during the deposition. A layer of 0.1 mm is deposited in approximately one minute. When the deposition process was completed, the substrate was cooled in the chamber at a temperature of 300°C with Argon which flows from the plasma gun anode opening. The cooled substrate with the tool is taken by the artificial arm and returned to its original position. The planetary system turns for one step, so that the artificial hand can accept another

tool with the substrate. The cycle of the powder deposition was repeated until the powder was not deposited on all the substrates. In this study, three groups of samples were made, with three distances of the powder deposition: 270, 295 and 320 mm. The coatings with thicknesses of 0.15 to 0.20 mm were formed. The other parameters were constant. The coating with the best structural and mechanical properties was tested on oxidation in the heat treatment furnace without protective atmosphere at 1100°C for a period of 240 hours.

Results and discussion

The measured values of the microhardness and the bond strength for deposited Co₃₂Ni₂₁Cr₈Al_{0.5}Y coatings depending on the plasma spray distance from the substrate are shown in Figures 3 and 4. The values of layer microhardness are directly related to the distance of the powder deposition. The plasma spray distances in the vacuum significantly influenced the values of microhardness and bond strength of the deposited layers. The highest value of microhardness of 615 HV_{0.3} was found in the layers deposited on the substrate with the lowest plasma spraying distance of 270 mm and with the lowest proportion of pores. The coating layers deposited with the highest distance of 320 mm had the lowest value of microhardness - 490 HV_{0.3}. The large distance from the substrate influenced the speed reduction and the subcooling of melted powder particles.

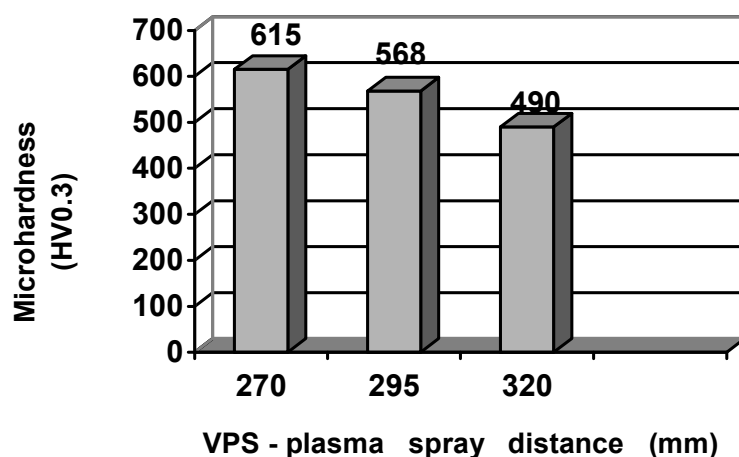


Figure 3 – Microhardness of Co₃₂Ni₂₁Cr₈Al_{0.5}Y layers
Slika 3 – Mikrotvrdoća Co₃₂Ni₂₁Cr₈Al_{0.5}Y slojeva

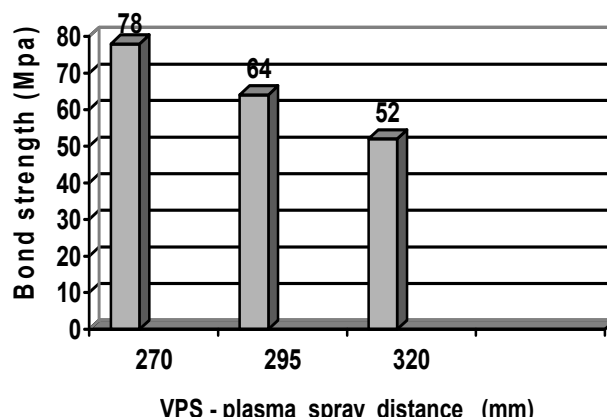


Figure 4 – Bond strength of Co32Ni21Cr8Al0.5Y layers
Slika 4 – Čvrstoća spoja Co32Ni21Cr8Al0.5Y slojeva

The result of a larger distance is reduced sagging of one particle to another and the formation of pores throughout the coating layers. These values were confirmed by the analysis of the coating microstructure by using light microscopy.

The comparison of the values of tensile bond strength, showed that good values of the bond strength were obtained for all three plasma spray distances. The cleaning of the substrate surface by the transferred arc resulted in better adhesion of the deposited coating layers, which then resulted in obtaining higher values of the bond strength. The bond strength of the coatings significantly depended on the plasma spraying distance. A lower value of the tensile bond strength of 52MPa of the coating deposited with the highest plasma spraying distance of 320 mm resulted in a lower degree of fusion of powder particles in comparison with other two deposited layers. The highest value of bond strength of 78MPa was found in the layers deposited with the shortest plasma spraying distance. These layers were the thickest. The tensile testing of the bond strength showed that in all deposited coatings, the mechanism of failure took place at the interface between the substrate and the coating. Since the proportion of pores and unmelted particles is directly related to the values of the bond strength of the coatings, these measured values for the deposited coating with the lowest plasma spraying distance indicate that their share is the lowest in comparison with two other coatings. These values were confirmed by the analysis of the microstructure of the coatings by using light microscopy. For all the deposited coating layers, the mechanism of failure was adhesion at the interface between the substrate and the coating.

Figures 5, 6 and 7 show the microstructures of the deposited layers on the substrates with a plasma spray distances of 270, 295 and 320 mm. The coating microstructures are in non-etched condition.

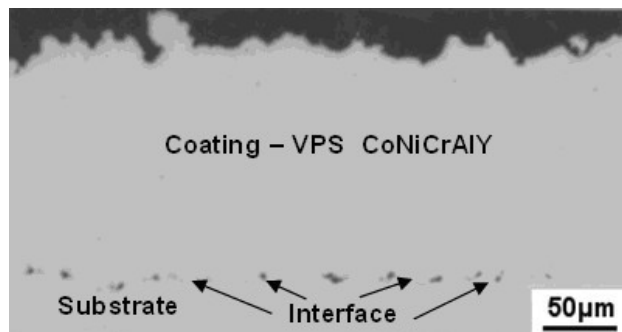


Figure 5 – Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating microstructure deposited on the sample with a substrate distance of 270 mm

Slika 5 – Mikrostruktura Co₃₂Ni₂₁Cr₈Al_{0.5}Y prevlake deponovane na uzorku sa odsto-
janjem substrata 270 mm

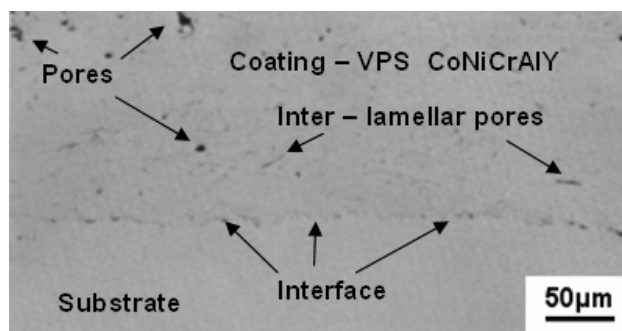


Figure 6 – Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating microstructure deposited on the sample with a substrate distance of 295 mm

Slika 6 – Mikrostruktura Co₃₂Ni₂₁Cr₈Al_{0.5}Y prevlake deponovane na uzorku sa odsto-
janjem substrata 295 mm

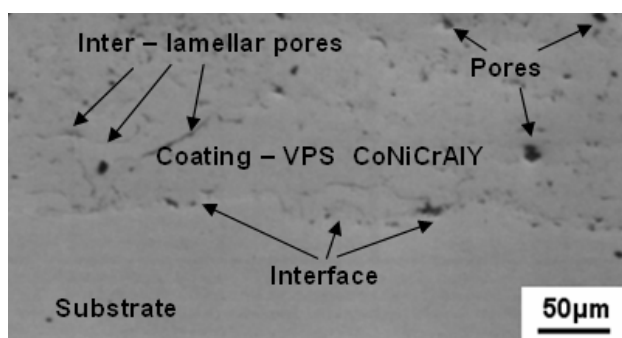


Figure 7 – Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating microstructure deposited on the sample with a substrate distance of 320 mm

Slika 7 – Mikrostruktura Co₃₂Ni₂₁Cr₈Al_{0.5}Y prevlake deponovane na uzorku
sa odstojanjem substrata 320 mm

The qualitative analysis showed that there are no defects on the interface between the substrate and the deposited coating such as discontinuity of the deposited layers on the substrate, microcracks, macrocracks and separation of the coating from the substrate. Figure 5 shows the layers of the deposited Co32Ni21Cr8Al0.5Y coating with the best structural and mechanical properties. The coating is thick and micropores cannot be observed through the layers, which is not the case with two other coatings. These layers are deposited onto the substrate with a plasma spraying distance of 270 mm continuously without interruption and without the presence of microcracks. Unmelted particles and precipitates are not present in the layers. The coatings deposited with a higher plasma spray distance have the presence of micropores of spherical and lamellar forms in their structure. The microstructures of the Co32Ni21Cr8Al0.5Y coating layers shown in Figures 6 and 7 show spherical and inter-lamellar pores marked with black arrows. These layers were deposited with a higher substrate distances of 295 mm and 320 mm from the plasma gun. Due to larger distances of the plasma gun, there was the subcooling of melted powder particles, which were, on impact with the substrate, less plastically deformed by forming spherical and inter-lamellar pores of black color. There are no unmelted powder particles and microcracks in the structure. Through all layers of the deposited coatings, oxide lamella cannot be noticed since the VPS - vacuum plasma spray process allows depositing of layers without the content of oxides in the coating, which is a huge advantage when compared to the APS - atmospheric plasma spray process. The largest proportion of spherical and inter-lamellar pores was found in the Co32Ni21Cr8Al0.5Y coating layers deposited with the highest plasma spraying distance of 320 mm. Because of the highest content of pores, these layers had the minimum value of microhardness and bond strength.

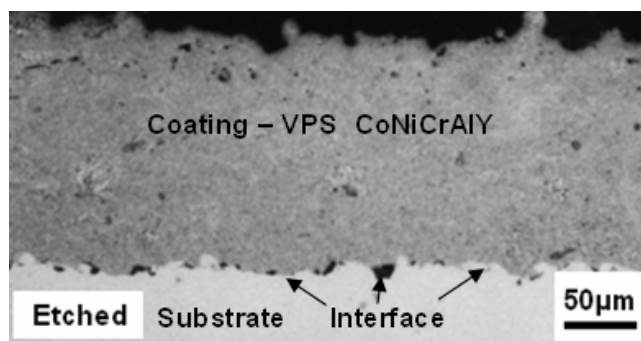


Figure 8 – Etched microstructure of the Co32Ni21Cr8Al0.5Y coating deposited on the sample with a substrate distance of 270 mm

Slika 8 – Nagrizena mikrostruktura Co32Ni21Cr8Al0.5Y prevlake deponovane na uzorku sa odstojanjem substrata 270 mm

The microstructures of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating deposited with a plasma spraying distance of 270 mm in etched condition with the best mechanical and structural characteristics, obtained by light microscopy, are shown in Figures 8 and 9.

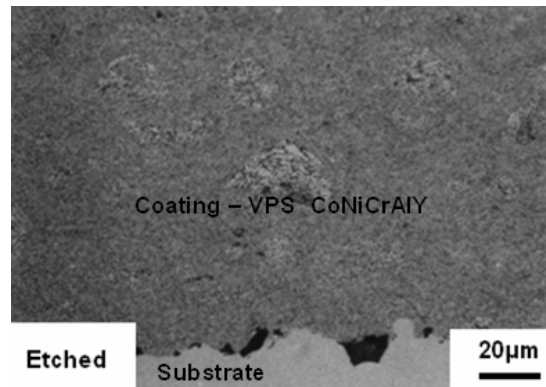


Figure 9 – Etched microstructure of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating deposited on the sample with a substrate distance of 270mm (higher magnification)

Slika 9 – Nagrizena mikrostruktura Co₃₂Ni₂₁Cr₈Al_{0.5} Y prevlake deponovane na uzorku sa odstojanjem substrata 270mm (više uvećanje)

In the microstructure of the coating there are two phases $\gamma + \beta$ which differ in color (Poza, Grant, 2006, pp.2887-2896), (Achar, et al., 2004, pp.272-283). The γ phase is light gray and the β phase is dark gray. The distribution of the phases in the microstructure is better seen in an SEM microphotography in Figure 10 where the coating is deposited with a plasma spraying distance of 270 mm.

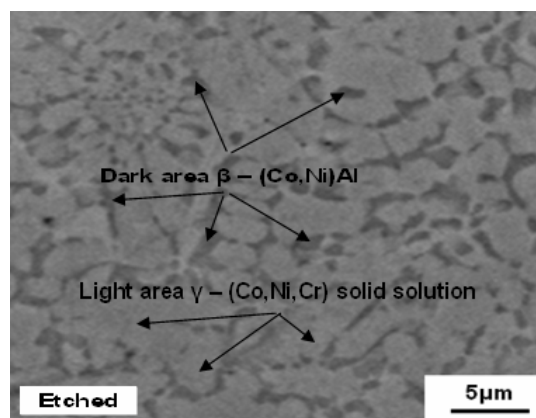


Figure 10 – (SEM) Etched microstructure of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating deposited on the sample with a substrate distance of 270 mm

Slika 10 – (SEM) Nagrizena mikrostruktura Co₃₂Ni₂₁Cr₈Al_{0.5}Y prvlake deponovane na uzorku sa odstojanjem substrata 270 mm

The SEM microphotography clearly shows two different phases that are marked with black arrows. The microstructure of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating layers consists of the basic γ solid solution of Co, Ni and Cr (light gray) in which the β (Co, Ni) Al phase (dark gray) is uniformly dispersed. The β phase rich in Al is formed from the β - CoAl and the β - NiAl phase (Poza, Grant, 2006, pp.2887-2896), (Achar, et al., 2004, pp.272-283), (Czech, et al., 1995, pp.28-33). Unmelted powder particles and precipitates are not present in the structure of the coating, which indicates rather uniform distribution of powder particles in the vacuum with respect to the atmospheric pressure.

Figure 11 shows the (SEM) microstructure of the coating tested on oxidation in a heat treatment furnace without protective atmosphere at 1100°C for a period of 240 hours. The anticipated changes occurred in the microstructure of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating in comparison with the coating microstructure in the deposited condition. The exposition of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating to 1100°C decreased the stability of the β (Co, Ni) Al phase because of Al diffusion.

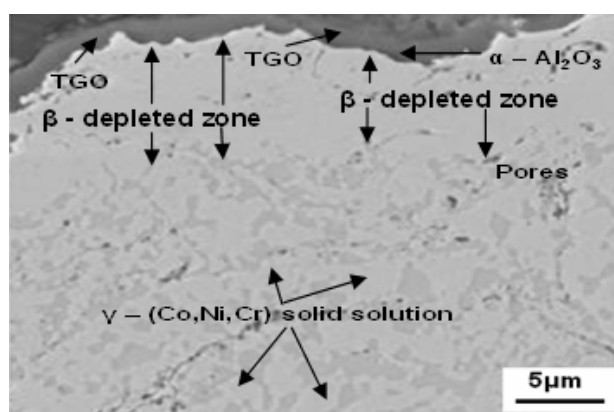


Figure 11 – SEM microphotography of the Co₃₂Ni₂₁Cr₈Al_{0.5}Y coating : oxidation at 1100°C/240 hours

Slika 11 – SEM mikrofotografija Co₃₂Ni₂₁Cr₈Al_{0.5}Y prevlake : oksidacija na 1100°C/240 sati.

Aluminium from the β phase filled the oxide layer on the coating surface and increased the thickness of the Al-depleted β – zone (light gray) marked with black arrows in Fig.11 (Cheruvu, et al., 2000, pp.50-54), (Mobarra, et al., 2006, pp.2202-2207). Besides α -Al₂O₃ oxide, the TGO zone was formed on the coating surface. In the TGO zone, besides the protective α - Al₂O₃ oxide, there are spinel compounds such as CoAl₂O₃ and NiAl₂O₃ or (Ni, Co) (Al, Cr)₂O₄ (Tang, et al., 2004, pp.228-

233). In the zone near the protective α - Al_2O_3 oxide layer and the TGO zone, there is no β (Ni, Co) Al phase, because the surface layer is Al-depleted (Nicholls, Bennett, 2000, pp.413–428). Only a small quantity of Al remained in the regions rich in (Ni, Co) (Leea, 2005, pp.239–242). In the area below the TGO zone there is the Al-depleted β –zone. The thickness of the depleted β – zone is from 5 to 8 μm , because of the long exposure of the coating to high temperature and due to the consumption of aluminum and the growth the TGO layer (Nicholls, Bennett, 2000, pp.413–428). In the lower layers of the coating, the untransformed light gray phase of the solid solution of γ - (Co, Ni and Cr) and the dark gray β (Co,Ni) Al phase are clearly evident. This indicates that the $\text{Co}_{32}\text{Ni}_{21}\text{Cr}_8\text{Al}_{0.5}\text{Y}$ coating did not degrade during 240 hours.

Conclusion

In this paper, the vacuum plasma spraying (VPS) process was used to deposit $\text{Co}_{32}\text{Ni}_{21}\text{Cr}_8\text{Al}_{0.5}\text{Y}$ coatings from the plasma gun at three distances of 270, 295 and 320 mm from the substrate. The structure and mechanical properties of the coatings were studied and analyzed in deposited condition as well as the influence of oxidation at 1100°C for a period of 240 hours on the microstructure of the deposited layers with the best characteristics, which led to the following conclusions.

The mechanical properties of the hardness and the bond strength of the coatings were directly related to the distance between the substrate and the plasma gun. Smaller distances of the substrate (270 mm) from the plasma gun gave the layers of coatings with higher microhardness and bond strength. Larger distances caused a formation of spherical and inter-lamellar pores through the coating layers; these pores resulted in lower values of the microhardness and the bond strength of these coatings. The mechanical properties of the coatings were in correlation with their microstructures.

The best microstructures were found in the layers deposited at a distance of 270 mm. These layers are dense and without the presence of micropores. The microstructure of the $\text{Co}_{32}\text{Ni}_{21}\text{Cr}_8\text{Al}_{0.5}\text{Y}$ layers of all deposited coatings is two-phase and consists of γ + β phases. The structure of the $\text{Co}_{32}\text{Ni}_{21}\text{Cr}_8\text{Al}_{0.5}\text{Y}$ coatings consists of the basic γ - (Co, Ni, Cr) solid solution (light gray), with the uniformly distributed β (Co, Ni) Al phase (dark gray).

After the heat treatment at 1100°C for a period of 240 hours, there was a change in the microstructure of the $\text{Co}_{32}\text{Ni}_{21}\text{Cr}_8\text{Al}_{0.5}\text{Y}$ coating in comparison with the coating in the deposited condition. Due to diffusion and oxidation of the elements at 1100°C, the structure of the primary β (Co, Ni) Al phase rich in Al becomes Al-depleted at the coating surface. Besides the α - Al_2O_3 oxide, the TGO zone is also formed at the coating

surface. Besides the protective α - Al_2O_3 oxide, the TGO zone contains spinel compounds such as CoAl_2O_3 and NiAl_2O_3 or $(\text{Ni}, \text{Co}) (\text{Al}, \text{Cr})_2\text{O}_4$ as a result of the diffusion of Co, Ni and Cr from the γ - solid solution. Below the TGO zone there is the Al-depleted β -zone in light gray. Lower coating layers still contain the untransformed γ - (Co, Ni and Cr) phase of the solid solution and the β (Co, Ni) Al phase. This indicates that, after 240 hours, the $\text{Co}_{32}\text{Ni}_{21}\text{Cr}_8\text{Al}_{10.5}\text{Y}$ coating proved to be resistant to high temperature oxidation at 1100°C for a period of 240 hours since it did not degrade.

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KARAKTERIZACIJA VAKUUM PLAZMA NAPRSKANE KOBALT-NIKAL-KROM-ALUMINIJUM-ITRIJUM PREVLAKA

OBLAST: hemijske tehnologije

VRSTA ČLANKA: originalni naučni članak

Sažetak:

U ovome radu je analiziran uticaj plazma sprej odstojanja na mikrostrukturu i mehaničke karakteristike Co32Ni21Cr8Al0.5Y prevlaka depnovanih vacuum plazma sprej postupkom (VPS). Mikrostruktura i meha-

ničke osobine plazma sprej prevlaka su određene interakcijom jona plazme Ar/H_2 sa česticama praha pri čemu nastaje prenos brzine i temperature jona na čestice praha. Efekat interakcije je u direktnoj zavisnosti od vremena interakcije jona i čestica praha koji je definisan plazma sprej odstojanjem. Prah je deponovan sa plazma pištoljem F4 sa tri odstojanja substrata 270, 295 i 320 mm. Prevlaka najboljih strukturnih i mehaničkih karakteristika je testirana na oksidaciju u peći za termičku obradu bez zaštitne atmosfere na 1100°C u trajanju od 240 sati. Morfologija čestica praha je ispitana na SEM-u. Mikrostruktura slojeva u deponovanom stanju je ispitana tehnikom svetlosne mikroskopije. Prevlaka najboljih mehaničkih karakteristikama je nagrizena elektrolitički sa 10% oksalne kiseline $\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$. Analiza mikrostrukture nagrizene prevlake je izvršena na svetlosnom mikroskopu i na SEM-u pre i posle testiranja prevlake na oksidaciju. Mikrostrukturna analiza deponovanih slojevima je urađena u skladu sa standardom Pratt-Whitney. Procena mehaničkih karakteristika slojeva je urađena ispitivanjem mikrotvrdoće metodom $\text{HV}_{0.3}$ i čvrstoće spoja ispitivanjem na zatezanje.

Uvod

Sistemi prevlaka CoNiCrAlY su razvijeni na osnovu sistema prevlaka NiCrAl , FeCrAlY , NiCrAlY i CoCrAlY (Mrdak, 2010, pp.5-16), (Mrdak, 2012, pp.182-201), (Driver, 2004), (Feuerstein, et al., 2008, pp.199-213). CoNiCrAlY su prevlake tipa koje se koriste u različitim aplikacijama gasnih turbina za zaštiti od visoko temperaturne oksidacije i tople korozije. Budući da su osobine i ponašanje prevlaka usko povezane sa mikrostrukturom, neophodno je da se ispituju strukture prevlaka posle depozicije i oksidacije na povišenim temperaturama (Gudmundsson, Jacobson, 1988, pp.207-217). Aluminijum u legurama CoNiCrAlY formira $\beta(\text{Co,Ni})\text{Al}$ fazu koja služi kao rezervoar za obnavljanje zaštitnog oksida $\alpha - \text{Al}_2\text{O}_3$. Legure na bazi Co sa aluminijumom proizvode $\beta - \text{CoAl}$ fazu koja poboljšava otpornost legure na sulfidizaciju i $\beta - \text{NiAl}$ fazu koja poboljšava otpornost legure na visoku temperaturnu oksidacionu.

Prevlake CoNiCrAlY često se deponuju plazma sprej postupkom u vakuumu (VPS). Glavna razlika je što se proces izvodi u vakuumu bez prisustva vazduha uz nizak pritisak u veoma čistim uslovima i uz primenu transferovanog luka za čišćenje površine substrata. U deponovanom stanju mikrostruktura CoNiCrAlY prevlake se sastoji od dve faze γ i β . γ faza je čvrst rastvor Co , Ni i Cr . $\beta(\text{Co,Ni})\text{Al}$ faza je formirana od $\beta - \text{CoAl}$ faze i $\beta - \text{NiAl}$ faze. Prisutna β faza i njen udeo u strukturi je od suštinskog značaja za zaštitu CoNiCrAlY prevlake. Radni vek CoNiCrAlY prevlake u uslovima oksidacije je u direktnoj vezi sa količinom β faze. Stabilnost $\beta(\text{Co,Ni})\text{Al}$ faze se smanjuje na visokim temperaturama zbog difuzije Al . Cheruvu i Mobarra sa saradnicima (Cheruvu, et al., 2000, pp.50 - 54), (Mobarra, et al., 2006, pp.2202-2207) su ustanovili da na visokim temperaturama Al iz β faze popunjava oksidni sloj na površini prevlake i siromaši β fazu sa Al . Izlaganjem CoNiCrAlY legure na 1100°C se na površini formira TGO zona sa zaštitnim oksid-

nim slojem α - Al_2O_3 . U zoni blizu zaštitnog oksidnog sloja α - Al_2O_3 nije prisutna β -(Ni,Co)Al faza jer je površinski sloj osiromašio sa Al (Nicholls, Bennett, 2000, pp.413-428). Samo mala količina Al ostaje u regionima bogatim (Ni,Co) (Leea, 2005, pp.239 - 242). U ovom području egzistira β - zona iscrpljena sa Al, koja se nalazi ispod gornjeg oksidnog TGO sloja. Debljina β - iscrpljene zone se povećava dužim izlaganjem legure na visokoj temperaturi zbog potrošnje aluminijuma i rasta TGO sloja (Nicholls, Bennett, 2000, pp.413-428). U TGO zoni, pored oksida α - Al_2O_3 , su prisutna i spinel jedinjenja kao što su CoAl_2O_3 i NiAl_2O_3 ili (Ni,Co)(Al,Cr) $_2\text{O}_4$ (Tang, et al., 2004, pp.228-233). Prevlake CoNiCrAlY u deponovanom stanju imaju visoku čvrstoću spoja od 55 - 62MPa (Material Product Data Sheet, 2011, DSMTS-0092.1, Sulzer Metco) i mikrotvrdoću $558 \pm 43 \text{ HV}_{0.3}$ za prosečnu vrednost poroznosti od 4.2%. Pored dobrih mehaničkih karakteristika, prevlake imaju nizak koeficijent trenja od 0.85 - 0,9 i otporne su na habanje (Gudmundsson, Jacobson, 1988, pp.207-217). Po preporuci proizvođača praha radna temperatura prevlaka CoNiCrAlY je $\leq 1050^\circ\text{C}$ (Material Product Data Sheet, 2011, DSMTS-0092.1, Sulzer Metco).

U radu su predstavljeni rezultati eksperimentalnih istraživanja uticaja sprej odstojanja na niskom pritisku na mehanička svojstva i mikrostrukturu slojeva Co32Ni21Cr8Al0.5Y prevlake. Urađene su tri grupe uzoraka sa tri različita odstojanja plazma pištolja 270, 295 i 320mm. Prevlaka sa najboljim karakteristikama je testirana na oksidaciju u peći za termičku obradu bez zaštitne atmosfere na 1100°C u trajanju od 240 sati. Glavni cilj rada je bio da se homologuju slojevi Co32Ni21Cr8Al0.5Y prevlake i primene na vazduhoplovnim delovima izloženim kombinaciji visoko temperaturne oksidacije i vrela korozije. Analizirane su mikrostrukture i mehaničke karakteristike slojeva prevlaka na osnovu čega se odabrala prevlaka najboljeg kvaliteta i homologovali vakuum plazma sprej parametri.

Materijali za ispitivanje i uzorci

Za eksperiment se koristio prah firme Sulzer Metco (Sulzer Metco) sa oznakom AMDRY 9951. Prah Co32Ni21Cr8Al0.5Y je razvijen za izradu prevlaka koje se koriste za zaštitu metalne osnove od visoko temperaturna oksidacije i vrela korozije na temperaturama $t \leq 1050^\circ\text{C}$ (Material Product Data Sheet, 2011, DSMTS-0092.1, Sulzer Metco). Metalni prah proizveden je atomizacijom tečnog rastopa legure Co32Ni21Cr8Al0.5Y inertnim gasnom argonom. Raspon granulacije čestica praha koji se koristio u eksperimentu bio je od 5 - $37\mu\text{m}$.

Osnove na koje su deponovane prevlake za ispitivanje mikrotvrdoće i za procenu mikrostrukture u deponovanom stanju su napravljene od čelika Č.4171 (X15Cr13 EN10027) u termički neobrađenom stanju dimenzija 70x20x1,5mm (Turbojet Engine - Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). Uzorci za ispitivanje mikrostrukture prevlake na oksidaciju na 1100°C su napravljeni od legure NIMONIC 80A dimenzija 70x20x1,5mm (Turbojet Engine - Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East

Hartford, USA). Osnove za ispitivanje čvrstoće spoja su takođe napravljene od čelika Č.4171(X15Cr13EN10027) u termički neobrađenom stanju dimenzija Ø25x50 mm (Turbojet Engine - Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

Ispitivanje mikrotvrdoće, čvrstoće spoja i mikrostrukture

Procena mehaničkih osobina slojeva je urađena ispitivanjem mikrotvrdoće metodom $HV_{0.3}$ i čvrstoće spoja ispitivanjem na zatezanje. Merenje mikrotvrdoće je izvršeno u pravcu duž lamela, u sredini i na krajevima uzoraka. Izvršeno je pet očitavanja vrednosti, koje su usrednjene.

Metoda ispitivanja čvrstoće spoja je metoda ispitivanja na zatezanje. Ispitivanje je urađeno na sobnoj temperaturi sa brzinom zatezanja 1cm/60s. Za svaku grupu uzoraka su ispitane po tri epruvete.

Morfologija čestica praha urađena je metodom SEM. Mikrostruktura slojeva u deponovanom stanju posle nagrivanja je ispitana tehnikom svetlosne mikroskopije. Prevlaka najboljih mehaničkih karakteristika, koja je termički tretirana na oksidaciju na 1100°C u trajanju od 240 sati ispitana je na skenirajućem elektronskom mikroskopu (SEM). Nagrivanje prevlake je rađeno elektrolitički sa 10% oksalne kiseline $H_2C_2O_4 \times 2H_2O$.

Depozicija praha

Depozicija praha izvršena je na niskom pritisku u vakuumu sa mešavinom plazma-gasova Ar- H_2 . Vakuum plazma sprej (VPS) sistem firme Plasma Technik AG je projektovan za zaštitu vazduhoplovnih delova izloženih kombinaciji prekomerne oksidacije i vrele korozije. U vakuum komori nalazi se: obrtni sto, planetarni sistem sa 48 alata, šestoosni robot i veštačka ruka. Sistem manipulacije projektovan je tako da istovremeno rotiraju alat i substrati oko svoje ose. Ovako složeno kretanje omogućava ravnomerno čišćenje transferovanim lukom i ravnomerno deponovanje praha po celoj površini substrata. U ovom istraživanju su urađene tri grupe uzoraka sa tri odstojanja depozicije praha 270, 295 i 320 mm. Prevlake su formirane sa debljinama od 0,15 do 0,20 mm. Ostali parametri bili su konstantni. Prevlaka najboljih strukturnih i mehaničkih karakteristika je testirana na oksidaciju u peći za termičku obradu bez zaštitne atmosfere na 1100°C u trajanju od 240 sati.

Rezultati i diskusija

Vrednosti mikrotvrdoće slojeva su u direktnoj vezi sa odstojanjem depozicije praha. Najveću vrednost mikrotvrdoće od 615 $HV_{0.3}$ su imali slojevi sa najmanjim udelom pora koji su deponovani na supstratu sa najmanjim plazma sprej odstojanjem od 270mm. Slojevi prevlake deponovani sa najvećim odstojanjem od 320 mm imaju najnižu vrednost mikrotvrdoće od 490 $HV_{0.3}$. Veliko odstojanje supstrata je uticalo na pothlađenje i smanjenje brzine istopljenih čestica praha.

Poređenjem vrednosti zatezne čvrstoće spoja, ustanovljeno je da su se za sva tri plazma sprej odstojanja dobile dobre vrednosti čvrstoće spoja. Čvrstoća spoja prevlaka je bitno zavisila od plazma sprej odstojanja. Niža vrednost zatezne čvrstoće spoja od 52MPa, prevlake deponovane sa najvećim plazma sprej odstojanjem od 320mm uticala je na manji stepen stapanja čestica praha u odnosu na druga dva deponovana sloja. Najveću vrednost čvrstoće spoja od 78MPa su imali slojevi, koji su deponovani sa najmanjim plazma sprej odstojanjem. Ti slojevi su se pokazali najgušćim. Ispitivanje zatezne čvrstoće spoja je pokazalo da se za sve deponovane prevlake mehanizam razaranja odvijao na interfejsu između substrata i prevlake. Pošto je udeo pora i neistopljenih čestica u direktnoj vezi sa vrednostima čvrstoće spoja prevlaka, to izmerene vrednosti za prevlaku deponovanu sa najmanjim plazma sprej odstojanjem ukazuje da je njihov udeo najmanji u odnosu na druge dve prevlake. Ove vrednosti su potvrđene analizom mikrostrukture prevlaka na svetlosnom mikroskopu.

Kvalitativna analiza je pokazala da na interfejsu između substrata i deponovanih prevlaka nisu prisutni defekti kao što je diskontinuitet deponovanih slojeva na supstratima, mikropukotine, makropukotine i odvajanje prevlaka od osnove. Na slici 5. su prikazani slojevi Co32Ni21Cr8Al0.5Y prevlake deponovane sa najboljom strukturnim i mehaničkim karakteristikama. Prevlaka je gusta i kroz slojeve se ne uočavaju mikropore, što nije slučaj za druge dve prevlake. Ti slojevi su deponovani na supstrat sa plazma sprej odstojanjem od 270mm kontinualno bez prekida i bez prisustva mikropukotina. U slojevima nisu prisutne nestopljene čestice i precipitati. Prevlake deponovane sa većim plazma sprej odstojanjem u strukturi pokazuju prisustvo mikropora sfernog i lamelnog oblika.

Na slikama 8 i 9 su prikazane, sa svetlosnog mikroskopa, mikrostruktura Co32Ni21Cr8Al0.5Y prevlake, deponovane sa plazma sprej odstojanjem od 270mm u nagriženom stanju sa najboljim mehaničkim i strukturnim karakteristikama. U mikrostrukturi prevlake se uočavaju dve faze $\gamma + \beta$ koje se razlikuju po boji (Poza, Grant, 2006, pp.2887-2896) (Achar, et al., 2004, pp.272-283). γ faza je svetlo sive boje a β faza tamno sive boje.

Na SEM mikrofotografiji jasno se uočavaju dve različite faze koje su obeležene crnim strelicama. Mikrostrukturu slojeva Co32Ni21Cr8Al0.5Y prevlake čini osnovni γ čvrst rastvor Co, Ni i Cr svetlo sive boje u kome je ravnomerno raspoređena β (Co, Ni) Al faza tamno sive boje. β faza bogata Al je formirana iz β - CoAl i β - NiAl faza (Poza, Grant, 2006, pp.2887-2896) (Achar, et al., 2004, pp.272-283), (Czech, et al., 1995, pp.28-33). U strukturi prevlake nisu prisutne neistopljene čestice praha i precipitati, što ukazuje na pravilnije razlivanje čestica praha u vakuumu u odnosu na atmosferski pritisak.

Na slici 11. je prikazana (SEM) mikrostruktura prevlake testirane na oksidaciju u peći za termičku obradu bez zaštitne atmosfere na 1100°C u trajanju od 240 sati. U mikrostrukturi Co32Ni21Cr8Al0.5Y prevlake došlo je do očekivajuće promene u poređenju sa mikrostrukturom prevlake u de-

ponovnom stanju. Izlaganjem Co32Ni21Cr8Al0.5Y prevlake na 1100°C smanjila se stabilnost $\beta(\text{Co,Ni})\text{Al}$ faze zbog difuzije Al. Aluminijum je iz β faze popunio oksidni sloj na površini prevlake i povećao debljinu β - zone iscrpljene sa Al svetlo sive boje označene crnim strelicama na sl.11 (Cheruvu, et al., 2000, pp.50 - 54), (Mobarra, et al., 2006, pp.2202-2207). Na površini prevlake pored oksida $\alpha\text{-Al}_2\text{O}_3$, formirala se i TGO zona. U TGO zoni, pored zaštitnog oksida $\alpha\text{-Al}_2\text{O}_3$, prisutna su i spinel jedinjenja kao što su CoAl_2O_3 i NiAl_2O_3 ili $(\text{Ni,Co})(\text{Al, Cr})_2\text{O}_4$ (Tang, et al., 2004, pp.228-233). U zoni blizu zaštitnog oksidnog sloja $\alpha\text{-Al}_2\text{O}_3$ i TGO zone nije prisutna $\beta(\text{Ni,Co})\text{Al}$ faza jer je površinski sloj iscrpljen sa Al (Nicholls, Bennett, 2000, pp.413-428). Samo je mala količina Al ostala u regionima bogatim (Ni,Co) (Leea, 2005, pp.239-242). U području ispod TGO zone egzistira β - iscrpljena zona sa Al. Debljina β - iscrpljene zone je od 5 - 8 μm zbog dugog izlaganja prevlake na visokoj temperaturi i zbog potrošnje aluminijuma i rasta TGO sloja (Nicholls, Bennett, 2000, pp.413-428). U donjim slojevima prevlake jasno se uočava netransformisana svetlo siva faza čvrstog rastvora γ - (Co,Ni i Cr) rastvora i tamno siva $\beta(\text{Co,Ni})\text{Al}$ faza. To ukazuje da se za 240 sati Co32Ni21Cr8Al0.5Y prevlaka nije degradirala.

Zaključak

U ovom radu, vakuum plazma sprej postupkom (VPS) su deponovane Co32Ni21Cr8Al0.5Y prevlake sa tri odstojanja 270, 295 i 320mm supstrata od plazma pištolja. Proučavane su i analizirane strukture i mehaničke karakteristike prevlaka u deponovanom stanju i uticaj oksidacije na 1100°C u trajanju od 240 sati na mikrostrukturu deponovanih slojeva sa najboljim karakteristikama, na osnovu čega se došlo do sledećih zaključaka.

Mehaničke osobine tvrdoće i čvrstoće spoja prevlaka su bile u direktnoj vezi sa odstojanjima supstrata od plazma pištolja. Sa manjim odstojanjem supstrata 270mm od plazma pištolja dobili su se slojevi prevlaka sa većom mikrotvrdoćom i čvrstoćom spoja. Veća odstojanja su uticala na formiranje sfernih i inter-lamelarnih pora kroz slojeve prevlaka, koje su uticale da se za te prevlake dobiju niže vrednosti mikrotvrdoće i čvrstoće spoja. Mehaničke karakteristike prevlaka su bile u korelaciji sa njihovim mikrostrukturama.

Najbolju mikrostrukturu su imali slojevi deponovani sa odstojanjem od 270mm. Ti slojevi su gusti i bez prisustva mikropora. Mikrostruktura Co32Ni21Cr8Al0.5Y slojeva svih deponovanih prevlake je dvofazna i sastoji se od $\gamma + \beta$ faza. Strukturu Co32Ni21Cr8Al0.5Y prevlaka čini osnovni γ - (Co,Ni,Cr) čvrst rastvor svetlo sive boje u kome je ravnomerno raspoređena $\beta(\text{Co,Ni})\text{Al}$ faza tamno sive boje.

U mikrostrukturi Co32Ni21Cr8Al0.5Y prevlake posle temperaturnog tretmana na 1100°C u trajanju od 240 sata došlo je do promene mikrostrukture u poređenju sa prevlakom u deponovanom stanju. Zbog difuzije i oksidacije elemenata na 1100°C, struktura primarne $\beta(\text{Co,Ni})\text{Al}$ faze bogate Al je na površini prevlake iscrpljena sa Al. Na površini prevlake se pored oksida $\alpha\text{-Al}_2\text{O}_3$ formirala i TGO zona. U

TGO zoni, pored zaštitnog oksida α - Al_2O_3 , prisutna su i spinel jedinjenja kao što su CoAl_2O_3 i NiAl_2O_3 ili $(\text{Ni},\text{Co})(\text{Al},\text{Cr})_2\text{O}_4$ kao posledica difuzije Co, Ni i Cr iz Y čvrstog rastvora. Ispod TGO zone prisutna je β – iscrpljena zona sa Al svetlo sive boje. U donjim slojevima prevlake i dalje je prisutna netransformisana γ -(Co, Ni i Cr) faza čvrstog rastvora i $\beta(\text{Co},\text{Ni})\text{Al}$ faza. To ukazuje da se za 240 sati $\text{Co}_{32}\text{Ni}_{21}\text{Cr}_8\text{Al}_{10.5}\text{Y}$ prevlaka pokazala otpornom na visokotemperaturnu oksidaciju na 1100°C u trajanju od 240 sata jer se nije degradirala.

Ključne reči: itrijum; vakuum; praškovi; plazma; čestice; mikrostruktura; automatizovati; mehaničke osobine; depoziti; prevlake.

Datum prijema članka/Paper received on: 03. 09. 2012.

Datum dostavljanja ispravki rukopisa/Manuscript corrections submitted on:
17. 03. 2013.

Datum konačnog prihvatanja članka za objavljivanje/ Paper accepted for publishing on:
19. 03. 2013.