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Characterization of deposited plasma spray $NiCrAlCoY_2O_3$ coating layers on AlMg1 alloy substrates

ABSTRACT

In this paper, analyzed are the effects of the plasma spray distance on the microstructure and mechanical properties of the $NiCrAlCoY_2O_3$ coating layers deposited at atmospheric pressure. The microstructure and mechanical properties of the coating layers are under the influence of the interaction of plasma particles (ions and electrons) with powder particles, providing the transfer of velocity and temperature of the plasma particles onto the powder particles. The effect of the interaction is directly dependent on the time the powder particles were present in the plasma which is defined by distance of the plasma gun from the substrate, depending on the granulation of the powder, the melting point and specific gravity. In order to obtain homogeneous and denser coating layers with high adhesion, in the experiment three distances from the substrate were used: 95 mm, 105 mm and 115 mm. The layers were deposited on thin sheets of AlMg1 aluminum thickness of 0.6 mm. Evaluation of mechanical properties of the layers was carried out by examining microhardness using the $HV_{0.1}$ method and the bond strength by tensile testing. The morphology of the powder particles was examined on the SEM, while the microstructure of the layers was evaluated under a light microscope in accordance with the Pratt Whitney standard.

The results of the experiment showed that the distance from the substrate substantially influenced the structure and mechanical properties of the coating layers. The best deposited layers were examined in the system with the $ZrO_2$24%MgO ceramic coating, which have proved to be reliable protectionfrom high temperature and abrasive rocket jet fuel.

Keywords: *atmospheric plasma spray (APS), microstructure, microhardness, bond strength*

1. INTRODUCTION

To protect substrates from the effects of gas corrosion and high temperature oxidation developed were nickel and cobalt based powders, type MeCrAlX (Me = Ni or Co, and X = Y or Hf) which were alloyed with metal components or as a composite - coated nickel-chrome powder with other metals or ceramics. One of the most dominant coated composite materials is $NiCr/Al/Co/Y_2O_3$ powder consisting of core particles of the NiCr alloy powder coated with fine micron particles of Al, Co and Y_2O_3 powders in the form of sheaths. The powders are deposited using plasma spray systems, as protective coatings or as bond coatings in combination with ceramic coatings (TBC thermal barrier coatings). When administered as bond layers they have a critical role in the performances of thermal barrier coatings for providing adhesion to the ceramic layers and resistance to oxidation and corrosion. Also, the deposited layers must be harmonized with the stress caused by sudden changes in temperature and substrate creep.

Protection of the substrate from gas corrosion and high temperature oxidation by MeCrAlY coatings (Me = Ni, Co or combinations there of) relies on the formation and maintaining of a continuous and thick α-Al_2O_3 oxide on the coating surface [1]. In the structure of the coating type

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NiCoCrAlYin deposited state present are stages: α - Al_2O_3,γ' - Ni_3Al and γ - Ni [1-3].

Resistance of the coatings deposited with composite powder is based on the formation of complex dual Al_2O_3-Y_2O_3 system oxides. The NiCr/Al/CoY_2O_3 powder coated with Y_2O_3 oxide increases the resistance of the NiCr alloy to oxidation because of the higher toughness of the complex oxides of the Al_2O_3-Y_2O_3 dual system that are formed in the process of the deposition of the powder. Figure 1 shows the phase diagram of the Al_2O_3-Y_2O_3 system. Depending on the mole fraction of the Al_2O_3 and Y_2O_3 oxides, in the structure of the coating oxides can occur as types: α-Al_2O_3, c-Y_2O_3,$YAlO_3$ (YAP), $Al_5Y_3O_{12}$ (YAG) and $Al_2Y_4O_9$ (YAM) [4]. The aim of coating the powder is so that the Al, in the process of deposition, reacts with the O from the atmosphere and forms an Al_2O_3 oxide which reacts with the Y_2O_3 from the powder forming complex oxides. Complex oxides are tougher compared to other types of oxides at high temperatures and resistant to stress caused by the difference in coefficients of linear and volumetric expansion at the interface surface / coating and coating / ceramic layer in two-layer systems.

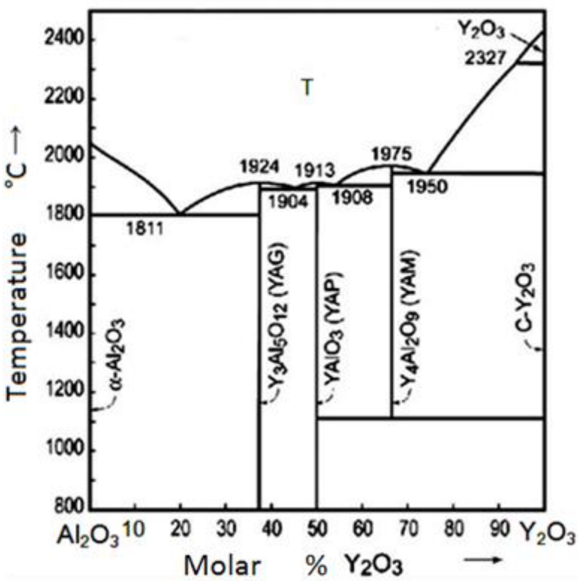

Figure 1. The phase diagram of Al_2O_3 - Y_2O_3

Slika 1. Fazni dijagram Al_2O_3 - Y_2O_3

Complex oxides in exploitation conditions slow downand prevent the penetration of oxygen in depth of the coating, because they are stable and ductile at high temperatures, which increase the cohesive strength of the NiCr lamellae. The base coating is made of a solid solution of γ-Ni(Cr) chromium in nickel. In the structure of the deposited layers, in addition to α-Al_2O_3 oxides present are complex oxides type $AlYO_3$(YAP), $Y_3Al_5O_{12}$(YAG) and Al_5YO_3, unmelted particles and micropores which together with the oxides have a significant impact on the microhardness and bond strength of the coating with the substrate [4-6]. An important advantage of the stable complex oxides is that at temperatures above 1000°C they prevent the transformation of the Cr_2O_3 oxide into CrO_3 which at this temperature evaporates. Consequently, these coatings are superior at high temperatures compared to all types of MeCrAlYalloys.

The main objective of this paper was to, by deposition of composite NiCr/Al/Co/Y_2O_3 powder on 0.6 mm thick AlMg1 alloy sheets, homologate coating layers and apply themas a bond coating in the system with the ceramic $ZrO_2$24%MgO coating on aviation crafts (airplane horizontal stabilizers) exposed to the combination of high temperature and abrasion in a short period of time while firing rockets. Three groups of samples were made with three plasma gun distances of 95 mm, 105 mm and 115 mm from the substrate. Analyzed and studied were the microstructures and mechanical properties of the NiCr/Al/Co/Y_2O_3 coating layers to select, based on the results, the best quality coatings and to homologate plasma spray parameters. The coatingwith the best microstructure and mechanical properties was applied in the system with the $ZrO_2$24%MgO coating, which while firing rockets showed dependable protection from the jet temperature and abrasive particles.

2. EXSPERIMENTAL PART

2.1. Materials and experimental details of plasma spray coatings deposition

For the experiment used was the powder of the company Oerlikon Metco marked Metco^{TM}461NS [7]. The powder was produced by the method of mechanical coating. The composite NiCr/Al/Co/Y_2O_3 powder used to make the bond layers consisted of NiCr alloy cores with (14.0-20.0)wt.%Cr, which were coated with (2.0-8.0)wt.%Al, (1.0-5.0)wt.%Co and (0.3-1.2)wt.%Y_2O_3. For the experiment used was a powder with granulation in therange of 45 µm to 150 µm [8]. The morphology of the powder particles was analyzed by scanning electron microscopy (SEM). Figure 2 shows the (SEM) photomicrograph of the NiCr/Al/Co/Y_2O_3 powder particles. The powder particles are of irregular shape with rough surfaces. In Table 1 shown are thermo-physical properties of the NiCr/Al/Co/Y_2O_3 coating and the substrate of ENAW-AlMg1(C)(ENAW-5005A) alloy at ambient temperature.

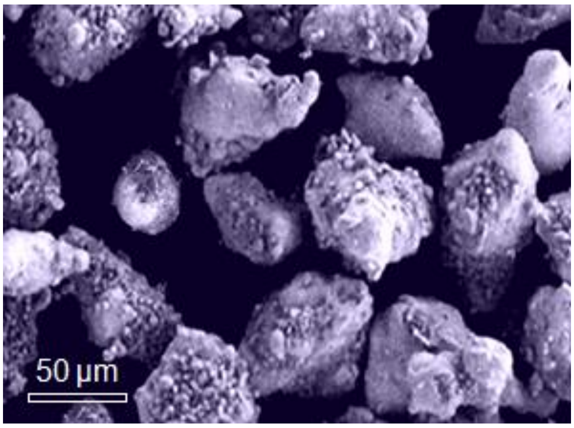

Figure 2. (SEM) The morphology of the $NiCr/Al/Co/Y_2O_3$ powder particles

Slika 2. (SEM) morfologija čestice praha $NiCrAlCoY_2O_3$

Table 1. Thermo-physical properties of the substrate and coating at ambient temperature [7]

Tabela 1. Termofizička svojstva podloge i prevlaka na temperaturi okoline [7]

Material	Thermal conductivity, W/mK	Coefficient of linear thermal expansoin, m/mK
$NiCr/Al/Co/Y_2O_3$	20 - 30	13×10^{-6}
AlMg1	203	$23{,}8\times10^{-6}$

For exploitation testing the quality of the $NiCr/Al/Co/Y_2O_3$ bond coating on substrates of aluminum alloy in a system with a ceramic coating the $ZrO_2$24%MgO powder was used with grain size of 10 µm to 53 µm [9]. In figure 3 shown is the (SEM) morphology of the $ZrO_2$24%MgO powder particles.

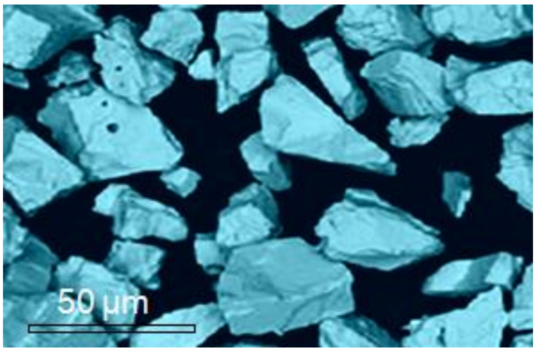

Figure 3. (SEM) the morphology of the $ZrO_2$24% MgO powder particles

Slika 3. (SEM) morfologija čestice praha $ZrO_2$24%MgO

The powder particles are of irregular shapes with sharp edges.

The bases on which the coating layers were deposited for micro-hardness testing and for evaluation of the microstructure in deposited state were made of ENAW-AlMg1(C)(ENAW-5005A) aluminum alloy 70x20x1.5mm in size. Bases for testing bond tensile strength were also made of ENAW-AlMg1(C)(ENAW-5005A) aluminum alloy Ø25x50 mm in size.

Testing of the microhardness of the layers was done using the $HV_{0.1}$ method. Microhardness measurement was carried out in the direction along the lamellae. Five readings of levels of microhardness of layers were done, in the middle and at the ends of the samples of which two extreme values were omitted. The paper presents the mean values of microhardness. The bond strengthof layers was tested by the tensile method at room temperature with a tensile speed of 1 mm/min.

For testing five paired specimens were used and the paper presents the mean values. The microstructure of a bond layers was investigated using optical microscopy (OM) according to the Pratt & Whitney standard [10].

The deposition of the $NiCr/Al/Co/Y_2O_3$ powder was carried out with the plasma spray system of the Plasmadyne Company and the SG-100 plasma gun, which is robotic with controlled plasma spray parameters. The plasma gun consisted of a K 1083-129 cathode, an A 2084-145 anode and a 2083-113 GI-type gas injector. As the arc, gas Ar was used in combination with He and power up to 40 kW. Before the process of depositing, the surface of the substrate of AlMg1 alloy was roughened with white corundum particles of 0.7 mm - 1.5 mmin size for greater reactivity of the surface and obtaining greater adhesion. Three groups of samples were done (A, B and C) with three distances of the plasma gun from the surface (95 mm, 105 mm and 115 mm). Plasma spray distance is one of the most important parameters affecting the quality of the coating because it is directly related to the adhesion - bond strength of the coating, cohesive strength and microhardness. Bond coatings were deposited with thicknesses of 0.6 mm to 0.12 mm. The ceramic $ZrO_2$24%MgO coating (CC) in a system with the bond coating for exploitation assessment was deposited with default, standard parameters [11]. The thickness of the ceramic coating was in the range of 0.3 to 0.35 mm. The deposition parameters of the coating layers are shown in Table 2.

Table 2. $NiCrAlCoY_2O_3$ and $ZrO_2$24%MgO powder deposition parameters

Tabela 2. Parametri depozicije praha $NiCrAlCoY_2O_3$ i $ZrO_2$24%MgO

Parameters	A	B	C	CC
Plasma current, I (A)	800	800	800	800
Plasma voltage, V (U)	38	38	38	43
Primary plasma gas flow rate, Ar (l/min)	48	48	48	50
Secondary plasma gas flow rate, He (l/min)	12	12	12	12
Carrier gas flow rate, Ar (l/min)	5	5	5	7
Powder feed rate, (g/min)	65	65	65	50
Stand-off distance, (mm)	95	105	115	90

3. RESULTS AND DISCUSSION

3.1. Results of coatings testing

The microhardness and tensile bond strength values of the deposited coating layers made of the composite NiCr/Al/Co/Y_2O_3 powder, depending on the plasma spray distance, are shown in Figures 4 and 5. The values of microhardness and bond strength of the deposited layers were significantly influenced by the distance of the plasma gun from the substrates. Figure 4 clearly shows that the values of microhardness of deposited layers were directly related to plasma spray distance. The layers deposited with the minimum distance of 95 mm had the minimum microhardness value of 256 $HV_{0.1}$. With a small distance of the plasma spray, the powder particles due to shorter retention in the plasma do not have enough time to fully melt, resulting in the increase in the portion of partially unmeleted particles and pores in the coating layers, which decrease the microhardness of the coating. By increasing distance to 105 mm the microhardness of the coating layers increases to 285 $HV_{0.1}$. The greatest value of microhardness of 342 $HV_{0.1}$ had layers deposited with the plasma spray distance of 115 mm. The higher microhardness values indicate that the powder particles in thedeposition process fully melted and that in the plasma jet the components of the NiCr/Al/Co/Y_2O_3 coating powder completely reacted, forming complex oxides, which was confirmed by metallographic examinationof the coating layers. These layers showed the best microstructure and densest packing of molten particles on each other with low content of pores.

Tensile bond strength as well as microhardness was directly related to the plasma spray distance. The minimum bond strength value of 26.3 MPa had the coating with the lowest microhardness, which was deposited from the plasma spray distance of 95 mm. Due to the higher content of unmelted and semi melted particles the coating achieved a weaker connection- adhesion to the substrate. With the increase of the distance to 105 mm the powder particles were increasingly melted, because of whichthey adhere better to the substrate and increase adhesion to 28.8 MPa.

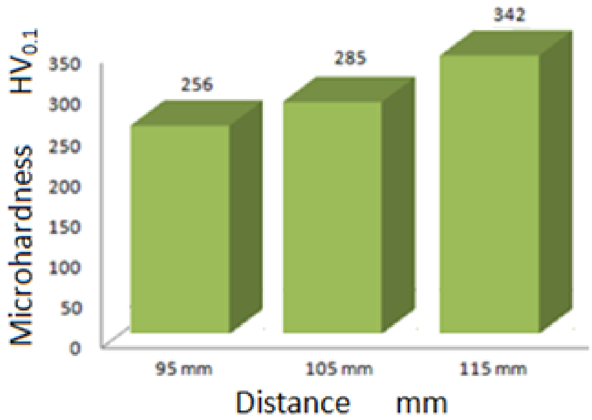

Figure 4. Microhardness of NiCr/Al/Co/Y_2O_3 layers

Slika 4. Mikrotvrdoća NiCr/Al/Co/Y_2O_3 slojeva

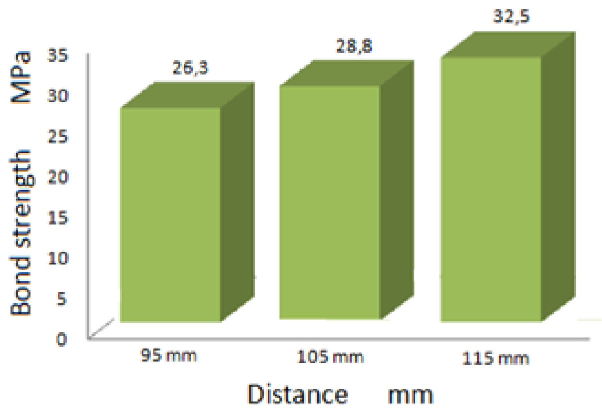

Figure 5. Bond strength of NiCr/Al/Co/Y_2O_3 layers

Slika 5. Čvrstoća spoja NiCr/Al/Co/Y_2O_3 slojeva

The highest value of bond strength of 32.5 MPa showed the layers having the greatest value of microhardness and the least share of pores, which were deposited at the plasma spray distance of 115 mm. High bond strength values and micro-hardness indicate that the melted powder particles were properly deformed on the substrate with a lamellar structure of the coating. The destruction mechanism for all deposited coatings was adhesion at the interface substrate / coating [12].

A qualitative analysis of the NiCr/Al/Co/Y_2O_3 coating showed that the layers were deposited on the substrates continuously without interruption and without the presence of microcracks at the interface substrate/coating. At the interface between coating and substrate there were no observed remains of corundum from roughening.

Figure 6 shows the microstructure of the NiCr/Al/Co/Y$_2$O$_3$ bond coating deposited at a plasma spray distance of 95 mm. In the structure of the coating clearly observed are unmelted powder particles which are surrounded by coarse micropores, black in color, indicating incomplete melting of the powder particles. Through the layers of the coating observedare black and dark gray lamellae of complex Al$_2$O$_3$-Y$_2$O$_3$ oxides at locations where there was complete melting of powder and the reaction of componentsof the coating powder, which in Figure 6 are marked with black arrows. On the surface of the bond coating the deposited ZrO$_2$24%MgO ceramic coating can be seen.

Uneven melting of the NiCr/Al/Co/Y$_2$O$_3$ powder particles with a high range of granulationfrom 45 µm to 150 µm resulted in uneven coating thickness along the substrate, which is clearly observed along the coating.

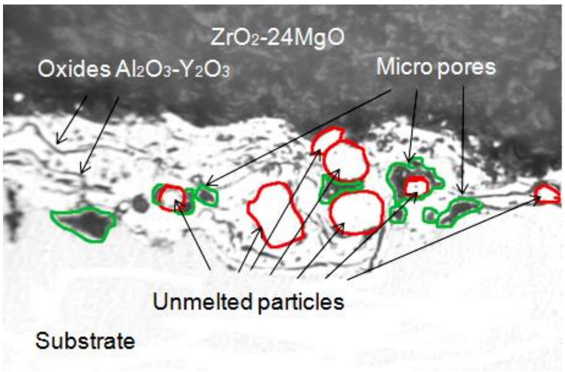

Figure 6. Microstructure of the NiCr/Al/Co/Y$_2$O$_3$ coating deposited at a distance of 95 mm

Slika 6. Mikrostruktura NiCr/Al/Co/Y$_2$O$_3$ prevlake deponovane na odstojanju od 95 mm

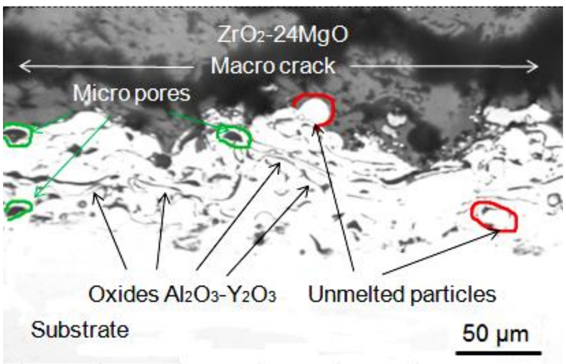

Figure 7. Microstructure of the NiCr/Al/Co/Y$_2$O$_3$ coating deposited at a distance of 105 mm

Slika 7. Mikrostruktura NiCr/Al/Co/Y$_2$O$_3$ prevlake deponovane na odstojanju od 105 mm

Figure 7 shows the structure of the NiCr/Al/Co/Y$_2$O$_3$ bond coating deposited at a plasma spray distance of 105 mm which clearly indicates that the thickness of the deposited layers is uniform along the coating with a smaller number of unmelted particles. The melted powder particles are deformed more properly and in the coating formed lamellae of the coating base made of NiCr alloy and lamellae of the Al$_2$O$_3$-Y$_2$O$_3$ complex oxides marked by arrows, which are located at the boundaries of the NiCr lamellae. In the top ZrO$_2$24%MgO ceramic layer a crackcan be seen, which extends parallel to the substrate, and is the result of cutting of the sample.

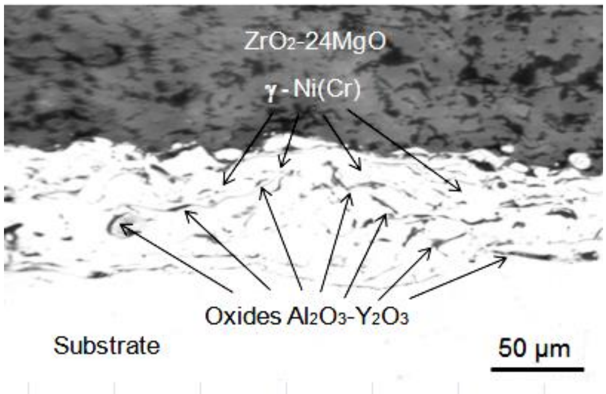

Figure 8. Microstructure of the NiCr/Al/Co/Y$_2$O$_3$ coating deposited at a distance of 115 mm

Slika 8. Mikrostruktura NiCr/Al/Co/Y$_2$O$_3$ prevlake deponovane na odstojanju od 115 mm

Figure 8 shows the NiCr/Al/Co/Y$_2$O$_3$ bond coating with the best microstructure which was deposited with a plasma spray distance of 115 mm. Due to the optimal melting of all powder particles this coating has the most uniform thickness. The layers are dense and homogeneous with a negligible proportion of micropores. The high degree of melting of the powder particles affected the reaction of Al with the Y$_2$O$_3$ from the powder. The melted aluminum from the powder reacts with melted yttrium oxide and forms an AlYO$_3$ (YAP) phase directly as per reaction:

$$3Al + Y_2O_3 = AlYO_3 + Al_2Y \quad (1)$$

Also, because of the primary Al$_2$O$_3$ oxide that is formed directly in the plasma as per reaction:

$$4Al + 3O_2 = 2Al_2O_3 \quad (2)$$

it reacts with melted Y$_2$O$_3$ and forms the Y$_3$Al$_5$O$_{12}$ (YAG) phase according to reaction:

$$5Al_2O_3 + 3Y_2O_3 \rightarrow 2Y_3Al5O_{12}\ (YAG) \quad (3)$$

The (YAG) phase can also be formed directly as per reaction:

$$3AlYO3 + Al_2O_3 \rightarrow Y_3Al_5O_{12} \quad (4)$$

During the melting of the powder in the plasma the $AlYO_3$ (YAP) and $Y_3Al_5O_{12}$ (YAG) phases are formed as primary oxides of the dual Al_2O_3-Y_2O_3 system [13-15].

The structure of the coating is lamellar with visible lamellae boundaries and with a good bond to the substrate. Basic longitudinal coating lamellae are light gray on the basis of NiCr alloy. The base of the lamellae consists of a solid solution of chromium in nickel γ-NiCr. Between the NiCr lamellae present are thin lamellar α-Al_2O_3 oxides and complex $AlYO_3$ (YAP) and $Y_3Al_5O_{12}$ (YAG) oxides of the dual Al_2O_3 -Y_2O_3 system [6,7]. Thin oxide lamellae are uniformly distributed along the boundaries of the NiCr lamellae in the whole base of the coating, which indicates that in some places the lamellae of the γ-NiCr solid solution are coated with oxides. In the coating layers, there is a negligible proportion of unmelted particles.

The coating with the best microstructure and mechanical properties was deposited in the system with $ZrO_2$24%MgO ceramic coatingon sections of airplane wings. Figure 9 shows one section.

Figure 9. Section of the wing of a plane with a coating NiCr/Al/Co/Y_2O_3/$ZrO_2$24%MgO

Slika 9. Sekcija krila aviona sa prevlakom NiCr/Al/Co/Y_2O_3/ $ZrO_2$24%MgO

When firing rockets there was no damage and deformation of the substrate and coating. Tests have shown that the dual coating system with the substrate was reliable protection from the jet temperature and abrasive particles, which allowed that the coating in the system with the substrate made of AlMg1 alloy was successfully applied to the rear horizontal stabilizers of a fighter plane.

4. CONCLUSIONS

In this paper, using atmospheric plasma spraying the composite–coated NiCr/Al/Co/Y_2O_3 powder particles were deposited on substrates of AlMg1 alloy with plasma spray distances of 95 mm, 105 mm and 115 mm.

Analyzed were the microstructure and mechanical properties of the layers, based on which the following conclusions were drawn.

Mechanical properties of the microhardness and bond strength and microstructure of the coating layers directly depended on the plasma spray distance.

The layers deposited with smaller plasma spray distances 95 mm and 105 mm, had lower values of the microhardness and bond strength, because of the brief period of the powder in the plasma causing less melting of the powder particles. Layers with the best mechanical and structural characteristics were obtained with plasma spray distance of 115 mm. These layers were homogeneous with a lamellar structure and dense with a negligible proportion of micropores, and thus had the highest values of microhardness and bond strength. During tensile testing the fracture mechanism was adhesion at the substrate / coating interface.

The basic structure of the best coating layers deposited with a plasma distance of 115 mm is made up of lamellae of a solid solution of chromium in nickel γ-NiCr. Along the boundaries of the NiCr lamellae formed were thin lamellae of α-Al_2O_3 oxide and complex $AlYO_3$(YAP) and $Y_3Al_5O_{12}$(YAG) oxides of the dual Al_2O_3-Y_2O_3 system.

The results showed that the plasma spray distance in the deposition process significantly affects the mechanical properties and microstructure of the coating layers.

Best layers that were deposited with a plasma distance of 115 mm were tested in the system with $ZrO_2$24%MgO ceramic coating which proved to be a reliable protection from the high temperature and abrasive rocket jet fuel..

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IZVOD

Karakterizacija deponovanih slojeva plazma sprej prevlake nicralcoy$_2$o$_3$ na podlogama od legure almg1

U ovome radu analiziran je uticaj plazma sprej odstojanja na mikrostrukturu i mehaničke karakteristike slojeva $NiCrAlCoY_2O_3$ prevlake deponovane na atmosferskom pritisku. Mikrostruktura i mehanička svojstva slojeva prevlake pod uticajem su interakcije čestica plazme (jona i elektrona) sa česticama praha, pri čemu nastaje transfer brzine i temperature čestica plazme na čestice praha. Efekat interakcije je u direktnoj zavisnosti od vremena boravka čestica praha u plazmi koji je definisan odstojanjem plazma pištolja od podloge zavisno od granulacije praha, temperature topljenja i specifične težine. U cilju dobijanja homogenih i gušćih slojeva prevlake visoke adhezije, u eksperimentu su korišćenja tri odstojanja od podloga: 95 mm, 105 mm i 115 mm. Slojevi su deponovani na tankim limovima od legure AlMg1 debljine 0,6 mm. Procena mehaničkih osobina slojeva je sprovedena ispitivanjem mikrotvrdoće metodom $HV_{0.1}$ i čvrstoće spoja ispitivanjem na zatezanje. Morfologija čestica praha je ispitana na SEM-u, dok su mikrostrukture slojeva procenjene na svetlosnom mikroskopu u skladu sa standardom Pratt-Whitney. Rezultati eksperimenta su pokazali da odstojanje podloga bitno utiče na strukturu i mehaničke karakteristike slojeva prevlaka. Najbolji deponovani slojevi su ispitani u sistemu sa keramičkom prevlakom $ZrO_2$24%MgO, koji su se pokazali kao pouzdana zaštuta od visokotemperaturnog i abrazivnog raketnog mlaza.

***Ključne reči**: atmosferski plazma sprej (APS), mikrostruktura, mikrotvrdoća, čvrstoća spoja.*

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