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Characterization of deposited plasma spray NiCrAlCoY₂O₃ 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 NiCrAlCoY₂O₃ 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 ZrO₂24%MgO ceramic coating, which have proved to be reliable protection from 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/Y₂O₃ powder consisting of core particles of the NiCr alloy powder coated with fine micron

particles of Al, Co and Y₂O₃ 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-Al₂O₃ oxide on the coating surface [1]. In the structure of the coating type

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NiCoCrAlYin deposited state present are stages: α - Al₂O₃, γ' - Ni₃Al and γ - Ni [1-3].

Resistance of the coatings deposited with composite powder is based on the formation of complex dual Al₂O₃-Y₂O₃ system oxides. The NiCr/Al/CoY₂O₃ powder coated with Y₂O₃ oxide increases the resistance of the NiCr alloy to oxidation because of the higher toughness of the complex oxides of the Al₂O₃-Y₂O₃ dual system that are formed in the process of the deposition of the powder. Figure 1 shows the phase diagram of the Al₂O₃-Y₂O₃ system. Depending on the mole fraction of the Al₂O₃ and Y₂O₃ oxides, in the structure of the coating oxides can occur as types: α -Al₂O₃, c-Y₂O₃, YAlO₃ (YAP), Al₅Y₃O₁₂ (YAG) and Al₂Y₄O₉ (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 Al₂O₃ oxide which reacts with the Y₂O₃ 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.

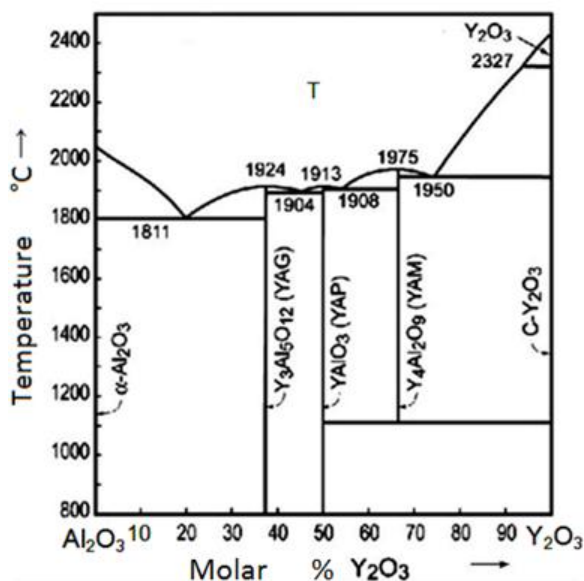


Figure 1. The phase diagram of Al₂O₃ - Y₂O₃

Slika 1. Fazni dijagram Al₂O₃ - Y₂O₃

Complex oxides in exploitation conditions slow down and 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 -Al₂O₃ oxides present are complex oxides type YAlO₃ (YAP), Y₃Al₅O₁₂ (YAG) and Al₅YO₃, 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 Cr₂O₃ oxide into CrO₃ which at this temperature evaporates. Consequently, these coatings are superior at high temperatures compared to all types of MeCrAlY alloys.

The main objective of this paper was to, by deposition of composite NiCr/Al/Co/Y₂O₃ powder on 0.6 mm thick AlMg1 alloy sheets, homologate coating layers and apply them as a bond coating in the system with the ceramic ZrO₂24%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/Y₂O₃ coating layers to select, based on the results, the best quality coatings and to homologate plasma spray parameters. The coating with the best microstructure and mechanical properties was applied in the system with the ZrO₂24%MgO coating, which while firing rockets showed dependable protection from the jet temperature and abrasive particles.

2. EXPERIMENTAL 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™461NS [7]. The powder was produced by the method of mechanical coating. The composite NiCr/Al/Co/Y₂O₃ 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.%Y₂O₃. For the experiment used was a powder with granulation in the range of 45 μ m to 150 μ m [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/Y₂O₃ 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/Y₂O₃ coating and the substrate of ENAW-AlMg1(C)(ENAW-5005A) alloy at ambient temperature.

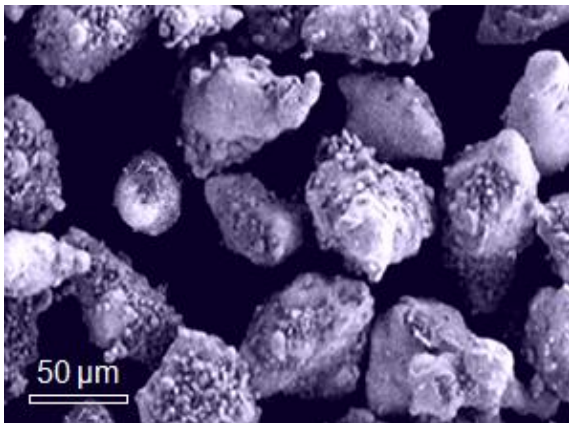


Figure 2. (SEM) The morphology of the NiCr/Al/Co/Y₂O₃ powder particles

Slika 2. (SEM) morfologija čestice praha NiCrAlCoY₂O₃

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 expansion, m/mK
NiCr/Al/Co/Y ₂ O ₃	20 - 30	13 × 10 ⁻⁶
AlMg1	203	23,8 × 10 ⁻⁶

For exploitation testing the quality of the NiCr/Al/Co/Y₂O₃ bond coating on substrates of aluminum alloy in a system with a ceramic coating the ZrO₂24%MgO powder was used with grain size of 10 μm to 53 μm [9]. In figure 3 shown is the (SEM) morphology of the ZrO₂24%MgO powder particles.

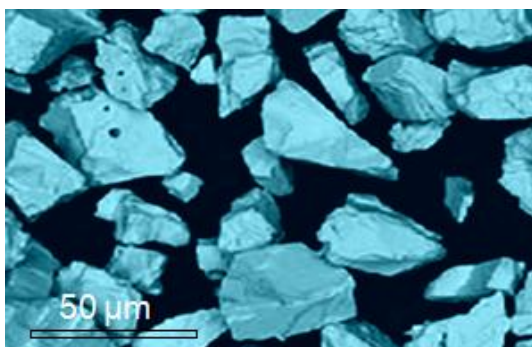


Figure 3. (SEM) the morphology of the ZrO₂24% MgO powder particles

Slika 3. (SEM) morfologija čestice praha ZrO₂24%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 strength of 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/Y₂O₃ 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 mm 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 ZrO₂24%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. NiCrAlCoY₂O₃ and ZrO₂24%MgO powder deposition parameters

Tabela 2. Parametri depozicije praha NiCrAlCoY₂O₃ i ZrO₂24%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/Y₂O₃ 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 unmeleated 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 the deposition process fully melted and that in the plasma jet the components of the NiCr/Al/Co/Y₂O₃ coating powder completely reacted, forming complex oxides, which was confirmed by metallographic examination of 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 which they adhere better to the substrate and increase adhesion to 28.8 MPa.

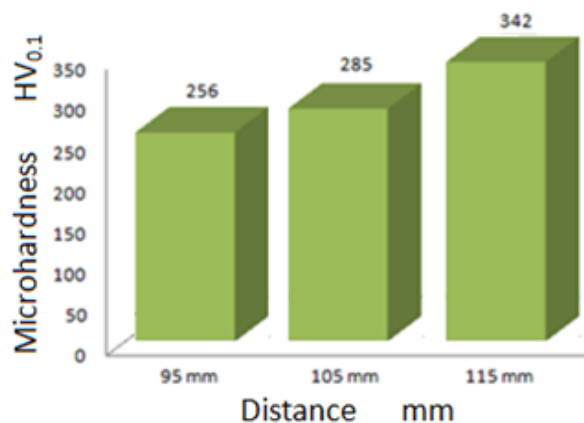


Figure 4. Microhardness of NiCr/Al/Co/Y₂O₃ layers

Slika 4. Mikrotvrdoća NiCr/Al/Co/Y₂O₃ slojeva

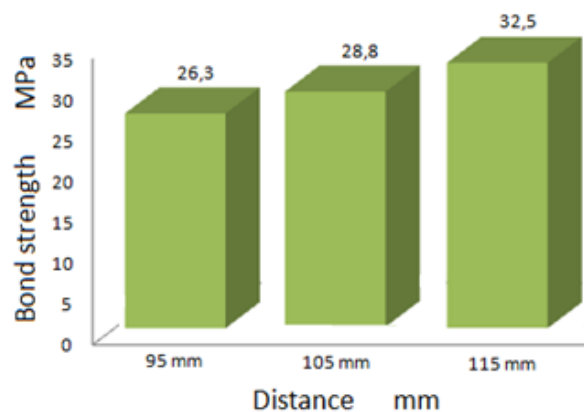


Figure 5. Bond strength of NiCr/Al/Co/Y₂O₃ layers

Slika 5. Čvrstoća spoja NiCr/Al/Co/Y₂O₃ 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 microhardness 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/Y₂O₃ 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/Y₂O₃ 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 observed are black and dark gray lamellae of complex Al₂O₃-Y₂O₃ oxides at locations where there was complete melting of powder and the reaction of components of the coating powder, which in Figure 6 are marked with black arrows. On the surface of the bond coating the deposited ZrO₂24%MgO ceramic coating can be seen.

Uneven melting of the NiCr/Al/Co/Y₂O₃ powder particles with a high range of granulation from 45 μm to 150 μm resulted in uneven coating thickness along the substrate, which is clearly observed along the coating.

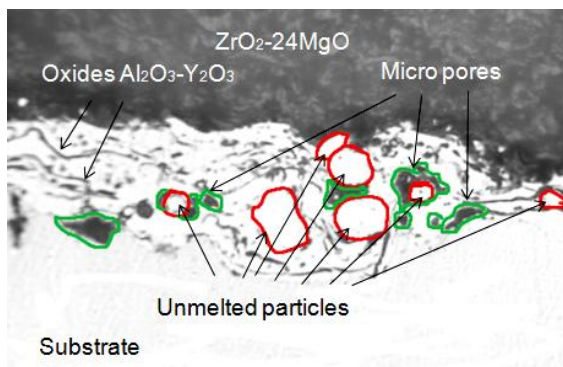


Figure 6. Microstructure of the NiCr/Al/Co/Y₂O₃ coating deposited at a distance of 95 mm

Slika 6. Mikrostruktura NiCr/Al/Co/Y₂O₃ prevlake deponovane na odstojanju od 95 mm

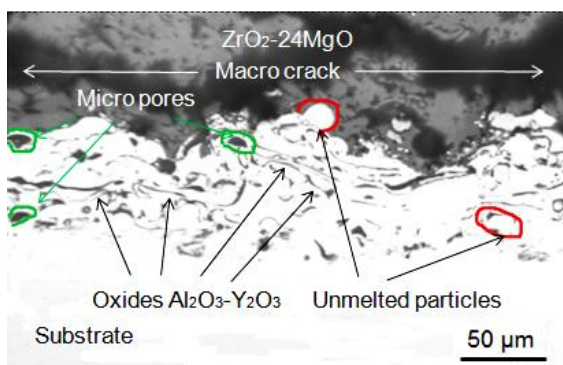


Figure 7. Microstructure of the NiCr/Al/Co/Y₂O₃ coating deposited at a distance of 105 mm

Slika 7. Mikrostruktura NiCr/Al/Co/Y₂O₃ prevlake deponovane na odstojanju od 105 mm

Figure 7 shows the structure of the NiCr/Al/Co/Y₂O₃ 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 Al₂O₃-Y₂O₃ complex oxides marked by arrows, which are located at the boundaries of the NiCr lamellae. In the top ZrO₂24%MgO ceramic layer a crack can be seen, which extends parallel to the substrate, and is the result of cutting of the sample.

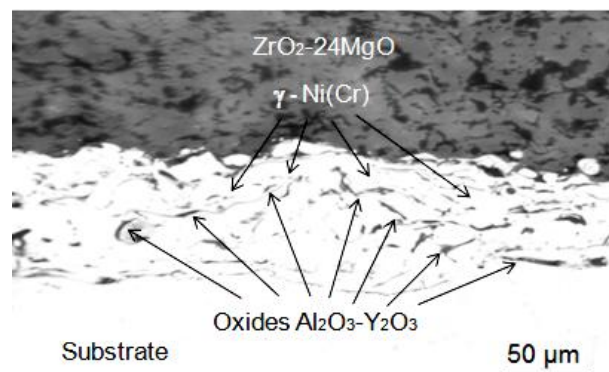


Figure 8. Microstructure of the NiCr/Al/Co/Y₂O₃ coating deposited at a distance of 115 mm

Slika 8. Mikrostruktura NiCr/Al/Co/Y₂O₃ prevlake deponovane na odstojanju od 115 mm

Figure 8 shows the NiCr/Al/Co/Y₂O₃ 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 Y₂O₃ from the powder. The melted aluminum from the powder reacts with melted yttrium oxide and forms an AlYO₃ (YAP) phase directly as per reaction:



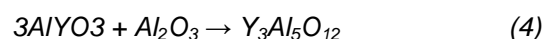
Also, because of the primary Al₂O₃ oxide that is formed directly in the plasma as per reaction:



it reacts with melted Y₂O₃ and forms the Y₃Al₅O₁₂ (YAG) phase according to reaction:



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



During the melting of the powder in the plasma the AlYO₃ (YAP) and Y₃Al₅O₁₂ (YAG) phases are formed as primary oxides of the dual Al₂O₃-Y₂O₃ 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 -Al₂O₃ oxides and complex AlYO₃ (YAP) and Y₃Al₅O₁₂ (YAG) oxides of the dual Al₂O₃-Y₂O₃ 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 ZrO₂24%MgO ceramic coating on sections of airplane wings. Figure 9 shows one section.



Figure 9. Section of the wing of a plane with a coating NiCr/Al/Co/Y₂O₃/ZrO₂24%MgO

Slika 9. Sekcija krila aviona sa prevlakom NiCr/Al/Co/Y₂O₃/ZrO₂24%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/Y₂O₃ 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 -Al₂O₃ oxide and complex AlYO₃(YAP) and Y₃Al₅O₁₂(YAG) oxides of the dual Al₂O₃-Y₂O₃ 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 ZrO₂24%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 DEPONOVAH SLOJEVA PLAZMA SPREJ PREVLAKE NiCrAlCoY₂O₃ NA PODLOGAMA OD LEGURE AlMg1

U ovome radu analiziran je uticaj plazma sprej odstojanja na mikrostrukturu i mehaničke karakteristike slojeva NiCrAlCoY₂O₃ 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 prevlake. Najbolji deponovani slojevi su ispitani u sistemu sa keramičkom prevlakom ZrO₂24%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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