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CHARACTERIZATION OF  
ALUMINUM OXIDE – 40%  
TITANIUMDIOXIDE COATING  
WEAR RESISTANT

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*Summary:*

*Plasma spray coatings play an important role in the design of surface properties of engineering components in order to increase their durability and performance under different operating conditions. Coatings are the most often used for wear resistance. This paper presents the microstructure and mechanical properties  $Al_2O_3$  40wt.%  $TiO_2$  coating resistant to dry friction slide, grain abrasion and erosion of particles at operating temperatures up to 540°C. In order to obtain the optimal characteristics of coating was performed optimization of deposition parameters. The powder  $Al_2O_3$  40wt.%  $TiO_2$  is deposited atmospheric plasma spraying (APS) process with a plasma current of 700, 800 and 900A. Evaluate the quality of the coating  $Al_2O_3$  40wt.%  $TiO_2$  were made on the basis of their hardness, tensile bond strength and microstructure. The best performance showed the deposited layers with 900A. The morphology of the powder particles  $Al_2O_3$  40wt.%  $TiO_2$  was examined with SEM (Scanning Electron Microscope). Microstructure of the coatings was examined by light microscopy. Analysis of the deposited layers was performed in accordance with standard Pratt & Whitney. Evaluation of mechanical properties of the layers was done by examining  $HV_{0.3}$  microhardness and tensile strength of the tensile testing. Studies have shown that plasma currents significantly affects the mechanical properties and microstructure of coatings which are of crucial importance for the protection for components subjected to wear.*

*Key word: titanium dioxide; aluminum oxide; bond strength; microhardness; interface; atmospheric plasma spray-APS.*

## Introduction

Plasma spray coatings are commonly used for the abrasion resistance of materials in many applications. Tribological performance coatings are dependent on a number of properties such as the composition of the powder, the nature of phases and their distribution, microstructure, porosity and residual stresses. All of these properties determine the hardness of coatings, which are conventionally used as the primary parameter for wear resistance. Mechanical properties of the coatings depend not only on the nature and distribution of the phases present in the coating, but also a number of other characteristics such as microstructure, porosity, nature of residual stresses and their value within the coating and adhesion of the coating. Coatings based on  $\text{Al}_2\text{O}_3$  ceramics are a good choice for protecting components subjected to excessive wear.  $\text{Al}_2\text{O}_3$  ceramic is hard and its main deficit is the brittleness (Ananthapadmanabhan, et al., 2003), (Erickson, et al., 2001). Adding titanium dioxide  $\text{TiO}_2$  leads to a balanced properties, maintain sufficient strength, but also a significant increase in toughness coating.  $\text{TiO}_2$  has a lower melting point than  $\text{Al}_2\text{O}_3$  and plays an important role in promoting the coatings with higher density (Pantelis, et al., 2000), (Gessasma, et al., 2006, pp.13-19), (Normand, et al., 2000, 278-287).  $\text{Al}_2\text{O}_3$ 40wt.% $\text{TiO}_2$  coatings is one of the coatings which are largely deposited atmospheric plasma spray process APS. It is known for its resistance to abrasion, corrosion and erosion. Control of the plasma spray process is considered to be very important in improving the characteristics of the deposit and the melting of the powder particles, mechanical properties of coatings and coating properties in service. In addition, hardness and tribological properties of coatings are strongly influenced by the deposition process parameters which directly affect the distribution of porosity and phase content of a range of particle size and morphology. Porosity in the coating decreases with increasing plasma current. With the reduction of plasma currents and increasing the flow of powder is present in the microstructure inhomogeneity such as porosity, cracks unmelted particles, oxide inclusions, which reduce the microhardness. (Vencl, et al., 2006, pp.151-157), (Mrdak, 2010, pp.5-16), (Mrdak, 2012, pp.182-201), (Mrdak, 2013, pp.68-88).  $\text{Al}_2\text{O}_3$ 40%wt. $\text{TiO}_2$  coatings deposited atmospheric plasma spray - APS has a porosity of 4 to 6% (Tomaszeka, et al., 2004, pp.137-149). The powder  $\text{Al}_2\text{O}_3$ 40%wt. $\text{TiO}_2$  consisting of oxide  $\text{Al}_2\text{O}_3$  and 40wt.% $\text{TiO}_2$ , which is used for the production of coatings for applications that require a moderate hardness and fracture strength greater than the strength of coatings produced from pure  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ 3wt.% $\text{TiO}_2$  ili  $\text{Al}_2\text{O}_3$ -13wt.% $\text{TiO}_2$  (Material Product Data Sheet, 2012, Amdry 6257 Aluminum Oxide 40% Titanium Dioxide Powders, DSMTS-0083.1, Sulzer Metco). The coatings  $\text{Al}_2\text{O}_3$ 40wt.% $\text{TiO}_2$  in the deposited state contains two modi-

fications  $\alpha$  –  $\text{Al}_2\text{O}_3$  and  $\gamma$  –  $\text{Al}_2\text{O}_3, \text{TiO}_2$  and two spinel modification of rutile  $\alpha$  –  $\text{Al}_2\text{TiO}_5$  and  $\beta$  –  $\text{Al}_2\text{TiO}_5$  (Tomaszeka, et al., 2004, pp.137-149), (Alford, 2002), (Vlasova, et al., 2012, pp.17-24). Coatings are recommended for surfaces bearing supports, for grain abrasion, friction and erosion of particles at operating temperatures up to 540°C. Polished coatings have low wettability, which makes them resistant to weak acid environment and suitable for use in the chemical processing industry (Material Product Data Sheet, 2012, Amdry 6257 Aluminum Oxide 40% Titanium Dioxide Powders, DSMTS-0083.1, Sulzer Metco). The coatings  $\text{Al}_2\text{O}_3\text{--TiO}_2$  provide excellent protection to the exposed parts of dry sliding friction, abrasive wear and erosion at high temperatures. The coefficients of thermal expansion of the coating  $\text{Al}_2\text{O}_3\text{--TiO}_2$  were 8 and 7.5 ( $10^{-6}\text{K}^{-1}$ ) (Normand, et al., 2000, pp.278-287). Such coatings are also desirable for electrical insulation, for protection axle sleeve and axle pumps. These coatings are generally resistant to abrasion, corrosion and thermal shock. With the addition of  $\text{TiO}_2$  coating increases wear resistance, tensile strength but the hardness decreases (Ramachandran, et al., 1998, pp.144-152). Titanium dioxide  $\text{TiO}_2$  has higher wear resistance with lower friction coefficient and lower hardness of  $\text{Al}_2\text{O}_3$  coatings. Wear behavior of atmospheric plasma sprayed (APS) coatings  $\text{Al}_2\text{O}_3\text{--TiO}_2$  tested using the method described in (Pin-On-Disk). The coefficient of friction decreases with an increasing sliding speed and applied load. In the initial period increases the coefficient of friction due to increased contact area and low surface roughness. Then the value of the coefficient of friction stabilizes (Krishnakumar, Swarnamani, 1996), (Guessasma, et al., 2006, pp.13-19). The coefficient of friction is determined by the method POD is 0.5-0.6 (Bounazef, et al., 2004, pp.2451-2455).

The main objective of this study was to atmospheric plasma spraying – APS deposited coatings  $\text{Al}_2\text{O}_3\text{--}40\text{wt.}\%\text{TiO}_2$  with the best structural and mechanical properties to be applied to aerospace parts bearing supports. Made three groups of samples with the current values of 700, 800 and 900 A. Analyzed and studied the microstructure and mechanical properties of layers of coatings. The best performance showed layers deposited with 900A.

## Materials and experimental details

For the experiment using powder company Sulzer Metco in terms Amdry 6257 (Material Product Data Sheet, 2012, Amdry 6257 Aluminum Oxide 40% Titanium Dioxide Powders, DSMTS-0083.1, Sulzer Metco). The powder  $\text{Al}_2\text{O}_3\text{--}40\text{wt.}\%\text{TiO}_2$  was developed for the preparation of coatings used for surface protection of bearings and supports the protection of the base metal friction, abrasion and erosion of particles up to 540°C. The powder was produced by melting and casting into blocks that are sub-

sequently milled to a specific granularity. This technological process to produce powders with angular grains. For the experiment using the powder granules had a range of 15–45 $\mu\text{m}$ . Figure 1 shows the (SEM) scanning electron micrographs of the morphology of the powder particles.

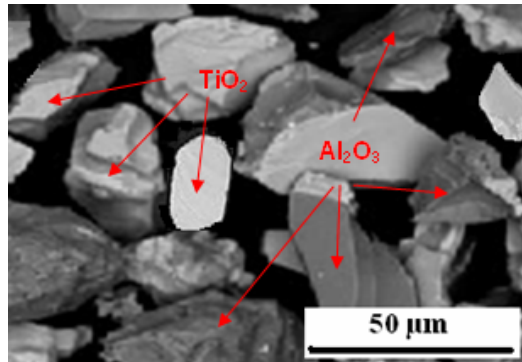


Figure 1 – (SEM) Scanning electron micrography of  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  powder particles  
Slika 1 – (SEM) Skening elektronska mikrografija čestica praha  $\text{Al}_2\text{O}_3$ –40%tež. $\text{TiO}_2$

On micrography seen angular grains of powder consisting of oxide  $\text{Al}_2\text{O}_3$  dark gray color and titanium dioxide  $\text{TiO}_2$  light gray. The bases on which the deposited coatings for testing microhardness and evaluation of microstructure in deposited state are made of steel Č.4171 (X15Cr13 EN10027) in thermally unprocessed dimensions of 70x20x1, 5mm (Turbojet Engine-Standard Practices Manual, 2002). Basis for testing the bond strength are also made of steel Č.4171 (X15Cr13EN10027) in thermally unprocessed dimension  $\varnothing 25 \times 50$  mm (Turbojet Engine-Standard Practices Manual, 2002).

## Microhardness testing, bond strength and microstructure

Examination of microhardness coating was performed by  $\text{HV}_{0.3}$ . The measurement was carried out in the direction along the fins in the middle and at the ends of the sample. Done five readings in three places, and the paper shows the minimum and maximum values.

Tests for tensile bond strength were performed at room temperature on hydraulic equipment with a speed of 10 mm / min, for all tests. For each group of samples were done three test specimen, and the paper presents the mean. Mechanical and microstructural characterization of the coating were carried out according to standard Pratt & Whitney (Turbojet Engine-Standard Practices Manual, 2002).

Microstructural analysis of the coating and image analysis of the share of micro pores in the coating was performed under a light microscope. The morphology of the powder particles was performed on the SEM (Scanning Electron Microscope).

## Powder deposition

Plasma spray deposition parameters are shown in Table 1 Powder deposition  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  was performed with an atmospheric plasma spray system company Plasmadyne and plasma gun SG – 100, with appropriate control robotic spray conditions. Plasma Gun SG -100 consisted of a cathode type K 1083-129, anode type A 2084-145 and gas injectors type GI 2083 – 113. As the arc gas was used Ar in combination with He and power supply up to 40 kW. Before the process of depositing steel substrate are roughed corundum particles with sizes of 0.7–1.5 mm. The coatings were formed with thicknesses from 0,25 to 0,30 mm.

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

Deposition parameters	Values		
	700	800	900
Plasma current, I (A)	700	800	900
Plasma Voltage, U (V)	36	38	40
Primary plasma gas flow rate, Ar (l/min)	47	47	47
Secondary plasma gas flow rate, He (l/min)	15	15	15
Carrier gas flow rate, Ar (l/min)	6	6	6
Powder feed rate (g/min)	50	50	50
Stand-off distance (mm)	110	110	110

## Results and discussion

The microhardness and microhardness ranges  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  coatings were directly related to the values of the plasma current. The layers  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  coatings were measured different values of microhardness with ones of various ranges. At least values of microhardness of min. 676 to max.734 $\text{HV}_{0.3}$  with the largest range of 58 $\text{HV}_{0.3}$  microhardness were observed in the deposited layers with values plasma current of 700A. The highest values of microhardness min. 950 to max 994 $\text{HV}_{0.3}$  to

the lowest range of  $44\text{HV}_{0.3}$  microhardness were observed in the deposited layers with values plasma current of 900A. Ranges microhardness of the coatings are the result of the different distribution of pores in the deposited layers. These values were confirmed by image analysis to determine the total content of pores in the layers. Figure 2 shown min. and max. values of the microhardness ceramic coatings  $\text{Al}_2\text{O}_3$ -40% wt. $\text{TiO}_2$ .

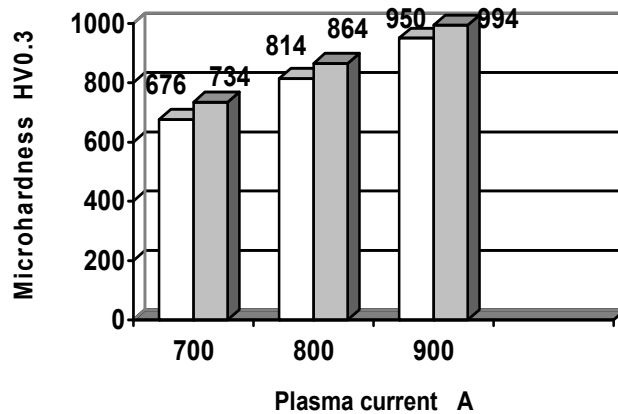


Figure 2 – Microhardness of  $\text{Al}_2\text{O}_3$ -40wt. $\text{TiO}_2$  layers  
Slika 2 – Mikrotvrdoća  $\text{Al}_2\text{O}_3$ 40%tež. $\text{TiO}_2$  slojeva

Figure 3 shows the values of tensile strength of  $\text{Al}_2\text{O}_3$ -40wt. $\text{TiO}_2$  coating. For the deposited coatings were measured for different values of tensile bond strength.

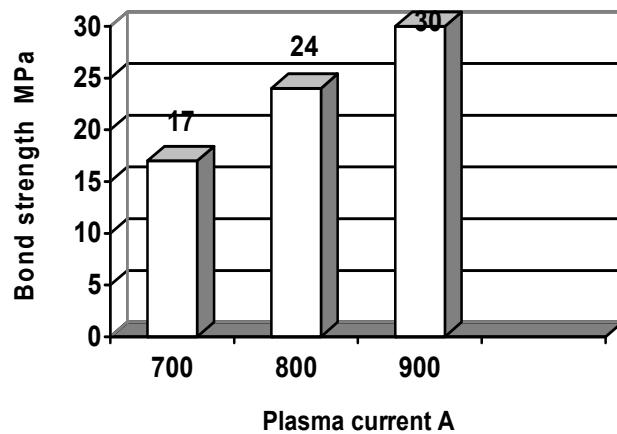


Figure 3 –  $\text{Al}_2\text{O}_3$ -40wt. $\text{TiO}_2$  bond strength layers  
Slika 3 – Čvrstoća spoja  $\text{Al}_2\text{O}_3$ -40%tež. $\text{TiO}_2$  slojeva

Bond strength coatings is significantly influenced by the value of the plasma current. The lowest tensile bond strength of 17MPa, coatings deposited with the lowest values of plasma current of 700A resulted in a lower degree of melting of the powder particles in comparison to the other two coatings deposited. The highest value of the bond strength of the 30MPa had layers that were deposited with the highest values of plasma current of 900A. The high value of the plasma current is allowed to deposit coatings with good inter – lamellar bonding and good bonding lamella for coating a substrate. A higher value of plasma current is increased the adhesion of coatings, mechanical properties and improvement of microstructure, as confirmed by metallographic examination. When the proportion of pores is directly related to the values of the bond strength of coatings, to the measured values of the coating deposited with the highest values of plasma current indicates that their rate of the lowest compared to the other two films. These values were confirmed by analyzing the microstructure of coatings under a light microscope. For all the deposited layer coating failure mechanism was adhesion at the interface between the substrate and the coating.

Microstructure and properties of coatings  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  were under the influence of the plasma current. A higher value of plasma current is because of an improved microstructure. Plasma currents of 900A provide better and more even melting of the powder particles  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$ . Evenly melted powder particles are more properly formed in the collision with the substrate and the deposited layers with a lower content of pores with higher cohesive strength and tensile strength. The minimum value of plasma current of 700A is influenced on less and limited bonding layers deposited in lamellae which increased the proportion of pores and reduce the coating hardness and adhesion of coating. On Figures 4 and 5 shows the microstructure of the deposited layers  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  coatings with values of plasma current 900A, which had the best microstructure and mechanical properties.

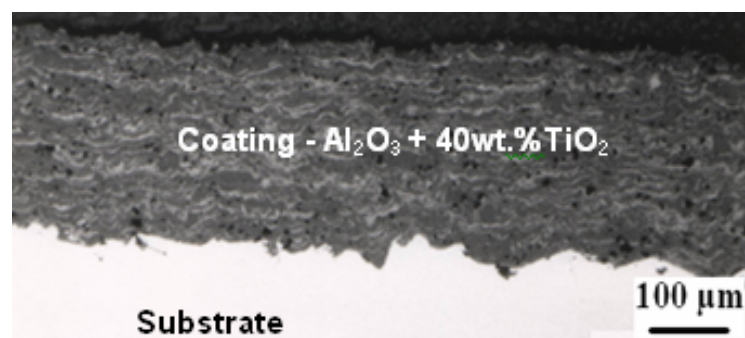


Figure 4 –  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  coating microstructure deposited with 900A  
Slika 4 – Mikrostruktura  $\text{Al}_2\text{O}_3$ 40%tež. $\text{TiO}_2$  slojeva prevlake deponovane sa 900A

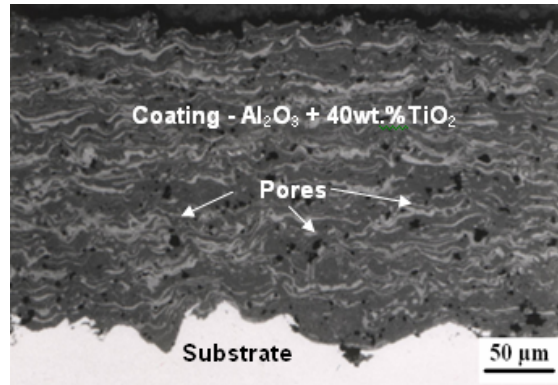


Figure 5 –  $\text{Al}_2\text{O}_3$ -40wt.% $\text{TiO}_2$  coating microstructure deposited with 900A  
Slika 5 – Mikrostruktura  $\text{Al}_2\text{O}_3$ -40%tež. $\text{TiO}_2$  slojeva prevlake deponovane sa 900A

Figure 4 shows the macro coatings  $\text{Al}_2\text{O}_3$ -40wt.% $\text{TiO}_2$  which confirms that uniform coating layers deposited on the substrate. Qualitative analysis of the deposited layers  $\text{Al}_2\text{O}_3$ -40wt.% $\text{TiO}_2$  (Figure 4 and Figure 5) showed that the interface between the substrate and the coating bond good with negligible content of particles  $\text{Al}_2\text{O}_3$  of roughening. Along the interface between the substrate and the coating are not present micro cracks and macro cracks. Bond coating with the substrate is uniform, without removing layers of coating with substrate. The structure of the coating is lamellar, with visible dark lamellae oxide  $\text{Al}_2\text{O}_3$  and light lamellae titanium dioxide  $\text{TiO}_2$ . Coating layers were deposited with a small rate of pores and microcracks in the absence of macro cracks in coating. The layers are not present unmelted powder particles.

Figure 6 shows the microstructure of the coatings deposited with the lowest values of plasma current 700A, which had the highest rate of pores and the worst mechanical properties.

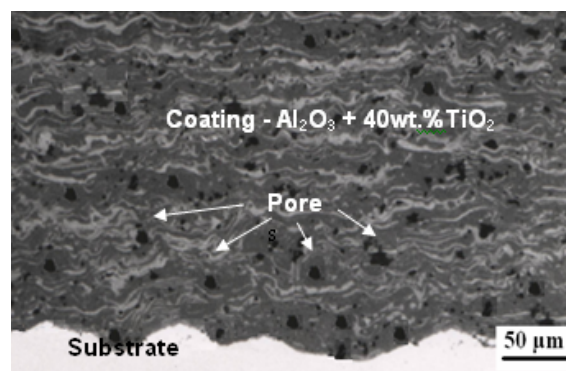


Figure 6 –  $\text{Al}_2\text{O}_3$ -40wt.% $\text{TiO}_2$  coating microstructure deposited with 700A  
Slika 6 – Mikrostruktura  $\text{Al}_2\text{O}_3$ -40%tež. $\text{TiO}_2$  slojeva prevlake deponovane sa 700A



Through the layers of coating are observed spherical pores black. In layers deposited with 900A micro pores are present up to 5  $\mu\text{m}$ . In layers deposited with 700A micro pores are present above 5  $\mu\text{m}$ . Image analysis showed that the overall rate of pores in the coating layers deposited with the 900A was 2%, In layers deposited with the 700A rate micro pores was 3.5%, and the deposited layers 800A rate of pores was 6%.

In Figure 7 shows the phases in the microstructure of coating with the best mechanical and structural characteristics.

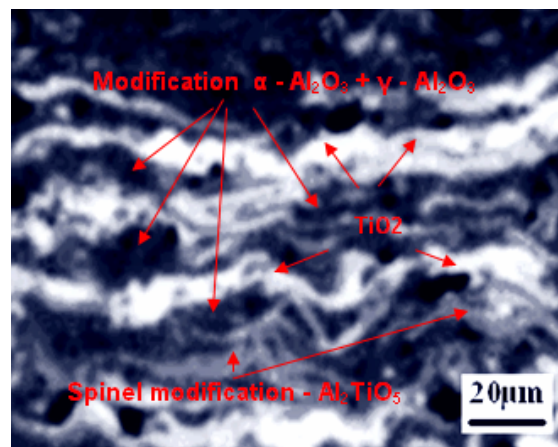


Figure 7 –  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$  coating microstructure deposited with 900A  
Slika 7 – Mikrostruktura  $\text{Al}_2\text{O}_3$ –40%tež. $\text{TiO}_2$  slojeva prevlake deponovane sa 900A

On photomicrograph shows that the molten powder particles regularly deposited. In microstructure not present unmelted particles and micro cracks. The structure of the inner layers of the coating is lamellar. The base coating is made of dark phase of basic oxide  $\text{Al}_2\text{O}_3$ . The structure of the present two modifications of  $\alpha$  -  $\text{Al}_2\text{O}_3$  and  $\gamma$  -  $\text{Al}_2\text{O}_3$  (Tomaszeka, et al., 2004, pp.137-149), (Alford, 2002), (Vlasova, et al., 2012, pp.17-24). Through ceramic layers of  $\text{Al}_2\text{O}_3$  phase is clearly observed light lamellae not degradable titanium dioxide  $\text{TiO}_2$  and two spinel modifications rutile of  $\alpha$  -  $\text{Al}_2\text{TiO}_5$  and  $\beta$  -  $\text{Al}_2\text{TiO}_5$  which are formed by reaction of oxides  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  powder melting process in the plasma (Tomaszeka, et al., 2004, pp.137-149), (Alford, 2002), (Vlasova, et al., 2012, pp.17-24).

## Conclusion

Plasma spraying coatings  $\text{Al}_2\text{O}_3$ –40%wt. $\text{TiO}_2$ were deposited with three different values of the plasma current 700, 800 and 900A. Examined and analyzed the microstructure and mechanical properties of the deposited coatings on the basis of which came to the following conclusions.

Mechanical properties and microstructure of coatings  $\text{Al}_2\text{O}_3$ -40% wt.  $\text{TiO}_2$  were under the influence of the plasma current. A higher value of plasma current is increased mechanical properties and improved adhesion of the coating microstructure.

With increasing plasma current were deposited the coatings by a higher values of microhardness and a smaller range of microhardness through layers coatings.

Coatings deposited with a plasma current of 900 A also had the highest values of microhardness and tensile bond strength. For all of coating failure was at the interface between the coating and the substrate. The microhardness and tensile bond strength were correlated with their microstructures.

The structure of the deposited coatings  $\text{Al}_2\text{O}_3$ -40%wt.  $\text{TiO}_2$  is lamellar. The coatings are present spherical pores black color. The smallest rate of micro pores than 2% had layers deposited with a plasma current of 900A, and the largest rate of micro pores of 6% had layers deposited with a plasma current of 700A. The structure of ceramic coatings  $\text{Al}_2\text{O}_3$ -40%wt.  $\text{TiO}_2$  present two modifications of aluminum oxide  $\alpha$  -  $\text{Al}_2\text{O}_3$  and  $\gamma$  -  $\text{Al}_2\text{O}_3$ , titanium dioxide  $\text{TiO}_2$  and two spinel modifications of rutile  $\alpha$  -  $\text{Al}_2\text{TiO}_5$  and  $\beta$  -  $\text{Al}_2\text{TiO}_5$  which are formed by reaction of oxides  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  powder melting process in the plasma.

### *Literature*

Ananthapadmanabhan, P.V., Thiyagarajan, T.K., Satpute, R.U., Venkatramani, N., Ramachandran, K., 2003, Surf Coat Technol., 168:231-40.

Alford, N.McN., EPSRC Final Report, No. GR/K70649, August 2002, available on <http://www.eeie.ac.uk/research/pem/reports%5cFINAL%20REPORT%20GRM33686.html>.

Bounazef, M., Guessasma, S., Ghislain, M., Christian, C., 2004, Effect of APS process parameters on wear behaviour of alumina – titania coatings, Materials Letters, Vol. 58, pp. 2451-2455.

Erickson, L.C., Hawthorne, H.M., Troczynski, T., 2001, Wear; 250:569-75.

Guessasma, S., Bounazef, M., Nardin, P., Sahraoui, T., 2006b, Note on POD test parameters to study wear behaviour of alumina – titania coatings, ceramics International, Vol.52, pp.13-19.

Krishnakumar, V. and Swarnamani, S., 1996, Tribological Behaviour of plasma sprayed  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  ceramic hard coating under dry contact., IIT Madras, department of applied Mechanics.

Material Product Data Sheet, 2012, Amdry 6257 Aluminum Oxide 40% Titanium Dioxide Powders, DSMTS-0083.1, Sulzer Metco.

Mrdak, M., 2010, Uticaj brzine depozicije praha na mehaničke karakteristike i strukturu APS – NiCr/Al prevlake, Vojnotehnički glasnik/Military Technical Courier, Vol.58, No.4, pp. 5-16.

Mrdak, M., 2012, Plasma deposited layers of nickel-chrome-aluminum-yttrium coatings resistant to oxidation and hot corrosion, *Vojnotehnički glasnik/Military Technical Courier*, Vol. 60, No.2, pp.182-201.

Mrdak, M., 2013, Characterization of sealing nickel-graphite coating in the system with bonding of nickel-aluminum coating, *Vojnotehnički glasnik/Military Technical Courier*, Vol. 61, No.1, pp.68-88.

Normand, B., Fervel, V., Coddet, C., Nikitine, V., 2000a, Tribological properties of plasma sprayed alumina-titania coatings:role and control of the microstructure, surface and coatings technology, Vol.123, pp.278-287.

Pantelis, DI., Psyllaki, P., Alexopoulos, N., 2000, *Wear*; 237:197-204.

Ramachandran, K., Selvarajan V., Ananthapadmanabhan P. V., Sreekumar K.P., 1998, Microstructure, adhesion, microhardness, abrasive wear resistance of the plasma sprayed alumina and alumina – titania coatings, *Thin solid film*, Vol. 315, pp.144-152.

Tomaszeka, R., Pawlowskia, L., Zdanowskib, J., Grimblotc, J., Laureynsd, J., 2004, Microstructural transformations of  $TiO_2$ ,  $Al_2O_3+13TiO_2$  and  $Al_2O_3+40TiO_2$  at plasma spraying and laser engraving, *Surface & Coatings Technology* 185, pp. 137-149.

Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA.

Vencl, A., Mrdak, M., Cvijović, I., 2006, Microstructures and tribological properties of ferrous coatings deposited by APS (Atmospheric Plasma Spraying) on Al-alloy substrate, *FME Transactions*, Vol.34, No.3, pp.151-157.

Vlasova, M., Kakazey, M., Sosa, B., Coeto, Marquez Aguilar, P. A., Rosales, I., Escobar Martinez, A., Stetsenko, V., Bykov, A., Ragulya, A., 2012, Laser Synthesis of  $Al_2TiO_5$  and  $Y_3Al_5O_{12}$  Ceramics from Powder Mixtures  $Al_2O_3-TiO_2$  and  $Al_2O_3-Y_2O_3$ , *Science of Sintering*, Vol.44, pp.17-24.

## KARAKTERIZACIJA ALUMINIJUM OKSID 40% TITANIJUM DIOKSID PREVLAKE OTPORNE NA HABANJE

OBLAST: hemijske tehnologije

VRSTA ČLANKA: originalni naučni članak

Sažetak:

*Plazma sprej prevlake predstavljaju važnu ulogu u projektovanju površinskih osobina inženjerskih komponenti u cilju povećanja njihove izdržljivosti i performansi pod različitim uslovima rada. Prevlake se najčešće koriste za otpornost na habanje. U radu su prikazane mikrostrukture i mehaničke karakteristike prevlake  $Al_2O_3-40tež.\%TiO_2$  otporne na suvo trenje klizanjem, abraziju zrna i eroziju čestica na radne temperature do  $540^{\circ}C$ . U cilju dobijanja optimalnih karakteristika prevlake izvršena je optimizacija parametara depozicije. Prah  $Al_2O_3-40tež.\%TiO_2$  je deponovan atmosferskim plazma sprej (APS) postup-*

kom sa plazma strujom od 700, 800 i 900A. Procene kvaliteta prevlake  $Al_2O_3$ -40tež. % $TiO_2$  su urađene na osnovu njihovih mikrotvrdoća, zatezne čvrstoće spoja i mikrostrukture. Najbolje performanse su pokazali slojevi deponovani sa 900A. Morfologija čestica praha  $Al_2O_3$ -40tež.% $TiO_2$  je ispitana na SEM-u (skening elektronskom mikroskopu). Mikrostruktura prevlaka ispitana je na svetlosnom mikroskopu. Analiza deponovanih slojevima je urađena u skladu sa standardom Pratt & Whitney. Procena mehaničkih karakteristika slojeva je urađena ispitivanjem mikrotvrdoće metodom  $HV_{0.3}$  i zatezne čvrstoće spoja ispitivanjem na zatezanje. Istraživanja su pokazala da plazma struja bitno utiče na mehaničke osobine i mikrostrukture prevlaka koje su od presudnog uticaja za zaštitu delova izloženih habanju.

#### Uvod

Plazma sprej prevlake se najčešće koriste za otpornost na habanje materijala u mnogim aplikacijama. Tribološke performanse prevlaka zavise od niza osobina kao što su: sastav praha, priroda faza i njihova raspodela, mikrostruktura, poroznost i zaostali naponi. Sve ove osobine određuju tvrdoću prevlaka, koja se konvencionalno koristi kao primarni parametar za procenu otpornost na habanje. Mehaničke osobine prevlake ne zavise samo od prirode i distribucije faza prisutnih u prevlaci, već i od niza drugih osobina kao što su mikrostruktura, poroznost, priroda zaostalih napona i njihova vrednost u okviru prevlake i adhezija prevlake. Prevlake na bazi  $Al_2O_3$  keramike su dobar izbor za zaštitu delova izloženih prekomernom habanju.  $Al_2O_3$  keramika je tvrda i njen glavni nedostatak je krtoš (Ananthapadmanabhan, et al., 2003), (Erickson, et al., 2001). Dodavanjem titanijum dioksida  $TiO_2$  dovodi do uravnoteženih svojstava, održavanja dovoljne tvrdoće, ali i značajnog povećanja žilavosti prevlake.  $TiO_2$  ima manju tačku topljenja od  $Al_2O_3$  i ima važnu ulogu u promovisanju prevlake sa većom gustinom (Pantelis, et al., 2000), (Gesasma, et al., 2006), (Normand, et al., 2000). Prevlaka  $Al_2O_3$ -40%tež. $TiO_2$  deponovana atmosferskim plazma sprejom - APS ima poroznost od 4 do 6% (Tomaszeka, et al., 2004, pp.137-149). Prah  $Al_2O_3$ -40%tež. $TiO_2$  se sastoji od oksida  $Al_2O_3$  i 40tež.% $TiO_2$  koji se koristi za proizvodnju prevlaka za aplikacije koje zahtevaju umerenu tvrdoću i veću čvrstoću preloma u odnosu na čvrstoću prevlaka proizvedenih od čistog  $Al_2O_3$ ,  $Al_2O_3$ -3tež.% $TiO_2$  ili  $Al_2O_3$ -13tež.% $TiO_2$  (Material Product Data Sheet, 2012, Amdry 6257 Aluminum Oxide 40% Titanium Dioxide Powders, DSMTS-0083.1, Sulzer Metco). Prevlaka  $Al_2O_3$ -40tež.% $TiO_2$  u deponovanom stanju sadrži dve modifikacije  $\alpha$  -  $Al_2O_3$  i  $\gamma$  -  $Al_2O_3$ ,  $TiO_2$  i dve spinel modifikacije rutila  $\alpha$  -  $Al_2TiO_5$  i  $\beta$  -  $Al_2TiO_5$  (Tomaszeka, et al., 2004, pp.137-149), (Alford, 2002), (Vlasova, et al., 2012, pp.17-24). Prevlake se preporučuju za površine oslonaca ležajeva, za otpornost na abraziju zrna, trenje i eroziju čestica na radne temperature do 540°C. Ove prevlake su generalno otporne na habanje, koroziju i toplotne udare. Sa dodatkom  $TiO_2$  povećava se otpornost prevlake na habanje, zatezna čvrdoća spoja ali se tvrdoća smanjuje (Ramachandran, et al., 1998,

pp. 144-152). Titanijum dioksid  $TiO_2$  ima veću otpornost na habanje, sa manjim koeficijentom trenja i manjom tvrdoćom od  $Al_2O_3$  prevlake. Ponašanje na habanje atmosferski plazma naprskane (APS) prevlake  $Al_2O_3TiO_2$  se ispituje pomoću metode POD (Pin-On-Disk). Koeficijent trenja se smanjuje sa povećanjem brzine klizanja i primenjenog opterećenja. U periodu uhodavanja se povećava koeficijent trenja zbog povećanja kontaktne površine i niže hrapavosti. Zatim se vrednost koeficijenta trenja stabilizuje (Krishnakumar, Swarnamani, 1996), (Guessasma, et al., 2006, pp. 13 -19). Koeficijent trenja određen metodom POD je 0.5-0.6 (Bounazef, et al., 2004, pp. 2451-2455).

Glavni cilj rada je bio da se atmosferskim plazma sprej postupkom – APS deponuju prevlake  $Al_2O_3$ –40tež.% $TiO_2$  sa najboljim strukturnim i mehaničkim karakteristikama koje će se primeniti na vazduhoplovnim delovima oslonaca ležajeva. Urađene su tri grupe uzoraka sa vrednostima struje od 700, 800 i 900 A. Analizirane su i proučavane mikrostrukture i mehaničke karakteristika slojeva prevlaka. Najbolje performanse su pokazali slojevi deponovani sa 900A.

#### Materijali i eksperimentalni detalji

Za eksperiment se koristio prah firme Sulzer Metco (Sulzer Metco) sa oznakom Amdry 6257 (Material Product Data Sheet, 2012, Amdry 6257 Aluminum Oxide 40% Titanium Dioxide Powders, DSMTS-0083.1, Sulzer Metco). Prah  $Al_2O_3$ –40%tež.% $TiO_2$  je razvijen za izradu prevlaka koje se koriste za zaštitu površine oslonaca ležajeva i zaštitu metalnih osnova od trenja, abrazije i erozije čestica do 540°C. Prah je proizveden metodom topljenja i livenja u blokove koji se naknadno melju na određenu granulaciju. Ovim tehnološkim postupkom se proizvode prahovi sa uglastim zrnima. Za eksperiment se koristio prah koji je imao raspon granulata od 15 - 45 $\mu$ 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). Osnove za ispitivanje čvrstoće spoja su takođe napravljene od čelika Č.4171(X15Cr13EN10027) u termički neobrađenom stanju dimenzija  $\varnothing$ 25x50 mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

#### Ispitivanje mikrotvrdoće, čvrstoće spoja i mikrostrukture

Ispitivanje mikrotvrdoće slojeva prevlaka urađeno je metodom  $HV_{0.3}$ . Merenje je obavljeno u pravcu duž lamela, u sredini i na krajevima uzorka. Urađeno je pet očitavanja na tri mesta, a u radu su prikazane minimalne i maksimalne vrednosti.

Ispitivanja zatezne čvrstoće spoja su rađena na sobnoj temperaturi na hidrauličnoj opremi sa brzinom od 10 mm/min, za sva ispitiva-

nja. Za svaki grupu uzoraka urađene su tri epruvete, a u radu su prikazane srednje vrednosti. Mehaničke i mikrostrukturne karakterizacije dobijenih prevlaka su izvršene prema standardu Pratt & Whitney (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

Mikrostrukturna analiza prevlaka i image analiza udela mikro pora u prevlakama urađena je na svetlosnom mikroskopu. Morfologija čestica praha urađena je na SEM-u (skening elektronskom mikroskopu).

#### Depozicija praha

Depozicija praha  $Al_2O_3-40\%tež.TiO_2$  je urađena sa atmosferski plazma sprej sistemom firme Plasmadyne i plazma pištoljem SG - 100, sa odgovarajućim robotizovanim kontrolnim sprej uslovima. Plazma pištolj SG -100 se sastojao od katode tipa K 1083 - 129, anode tipa A 2084 - 145 i gas injektora tipa GI 2083 - 113. Kao lučni gas koristio se Ar u kombinaciji sa He i snaga napajanja do 40 KW. Pre procesa deponovanja površine čeličnih substrata su hrapavljene sa česticama konda veličine od 0,7 - 1,5 mm. Prevlake su formirane sa debljinama od 0.25-0.30 mm.

#### Rezultati i diskusija

Vrednosti mikrotvrdoće i rasponi mikrotvrdoće  $Al_2O_3-40\%tež.TiO_2$  prevlaka su bile u direktnoj vezi sa vrednostima plazma struje. U slojevima  $Al_2O_3-40\%tež.TiO_2$  prevlaka izmerene su različite vrednosti mikrotvrdoće sa različitim rasponima mikrotvrdoća. Najmanje vrednosti mikrotvrdoće od min.676 do max.734HV<sub>0.3</sub> sa najvećim rasponom mikrotvrdoće od 58HV<sub>0.3</sub> su izmerene u deponovanim slojevima sa vrednostima plazma struje od 700A. Najveće vrednosti mikrotvrdoće od min.950 do max.994HV<sub>0.3</sub> sa najmanjim rasponom mikrotvrdoće od 44HV<sub>0.3</sub> su izmerene u deponovanim slojevima sa vrednostima plazma struje od 900A. Rasponi mikrotvrdoće u prevlakama su posledica različite raspodele mikro pora u deponovanim slojevima. Ove vrednosti su potvrđene image analizom pri određivanju ukupnog sadržaja mikro pora u slojevima.

Za deponovane prevlaka su izmerene različite vrednosti zatezne čvrstoće spoja. Čvrstoća spoja prevlaka je bitno zavisila od vrednosti plazma struje. Najniža vrednost zatezne čvrstoće spoja od 17MPa, prevlake deponovane sa najmanjom vrednosti plazma struje od 700A uticala je na manji stepen stapanja čestica praha u odnosu na druge dve deponovane prevlake. Najveću vrednost čvrstoće spoja od 30MPa su imali slojevi, koji su deponovani sa najvećom vrednosti plazma struje od 900A. Visoka vrednost plazma struje je omogućila da se deponuju prevlake sa dobrim među – lamelarnim vezivanjem i dobrim vezivanjem lamela prevlake za substrat. Veća vrednost plazma struje je uticala na povećanje adhezije prevlaka, mehaničkih svojstava i poboljšanje mikrostrukture, što su potvrdila metalografska ispitivanja. Pošto je udeo mikro

pora u direktnoj vezi sa vrednostima čvrstoće spoja prevlaka, to izmerene vrednosti za prevlaku deponovanu sa najvećom vrednosti plazma struje ukazuje da je njihov udeo najmanji u odnosu na druge dve prevlake. Ove vrednosti su potvrđene analizom mikrostrukture prevlaka na svetlosnom mikroskopu. Za sve deponovane slojeve prevlaka mehanizam razaranja je bio athezioni na interfejsu između substrata i prevlaka.

Mikrostrukture i svojstava  $Al_2O_3$ –40%tež. $TiO_2$  prevlaka su bila pod uticajem plazma struje. Veća vrednost plazma struje je poboljšala mikrostrukturu. Plazma struja od 900A omogućila je bolje i ravnomernije topljenje čestica praha  $Al_2O_3$ –40%tež. $TiO_2$ . Ravnomerno istopljenje čestice praha su se pravilnije oblikovale u sudaru sa substratom i deponovale slojeve sa manjim sadržajem mikro pora, koji imaju veću kohezionu čvrstoću i zateznu čvrstoću spoja. Najmanja vrednost plazma struje od 700A je uticala na slabije i ograničeno vezivanje lamela u deponovanim slojevima što je povećalo udeo mikro pora i smanjilo vrednosti tvrdoće prevlake i čvrstoću spoja prevlake. Kvalitativna analiza deponovanih  $Al_2O_3$ 40%tež. $TiO_2$  slojeva je pokazala da je na interfejsu između substrata i prevlake spoj dobar sa zanemarljivim sadržajem čestica  $Al_2O_3$  od hrapavljenja. Duž interfejsa između substrata i prevlake nisu prisutne mikropukotine i makropukotine. Veza prevlake sa substratom je uniformna bez odvajanja slojeva prevlake sa substrata. Struktura prevlake je lamelarna, sa vidljivim tamnim lamelama oksida  $Al_2O_3$  i svetlim lamelama titanijum dioksida  $TiO_2$ . Slojevi prevlake su deponovani sa malim udelom mikro pora bez prisustva mikropukotina i makropukotina u uprevlaci. U slojevima nisu prisutne neistopljene čestice praha. Kroz slojeve prevlaka se uočavaju sferne pore crne boje. U slojevima deponovanim sa 900A su prisutne mikro pore veličine do 5  $\mu m$ . U slojevima deponovanim sa 700A su prisutne mikro pore iznad 5  $\mu m$ . Image analiza je pokazala da je ukupan udeo mikro pora u slojevima prevlake deponovane sa 900A bio 2%, u slojevima deponovanim sa 700A udeo mikro pora je bio 3.5%, a u slojevima deponovanim sa 700A udeo mikro pora je bio 6%. U mikrostruktri nisu prisutne neistopljene čestice i mikroprskotine. Struktura unutrašnjih slojeva prevlake je lamelarna. Osnova prevlake se sastoji od tamne faze osnovnog oksida  $Al_2O_3$ . U strukturi su prisutne dve modifikacije  $\alpha$  -  $Al_2O_3$  i  $\gamma$  -  $Al_2O_3$  (Tomaszeka, et al., 2004, pp.137-149), (Alford, 2002), (Vlasova, et al., 2012, pp.17-24). Kroz keramičke slojeve  $Al_2O_3$  faza jasno se uočavaju svetle lamele nerazgrađenog titanijum dioksida  $TiO_2$  i dve spinel modifikacije rutila  $\alpha$  -  $Al_2TiO_5$  i  $\beta$  -  $Al_2TiO_5$  koje se formiraju reakcijom oksida  $Al_2O_3$  i  $TiO_2$  u procesu topljenja praha u plazmi (Tomaszeka, et al., 2004, pp.137-149), (Alford, 2002), (Vlasova, et al., 2012, pp.17-24).

#### Zaključak

Plazma sprej postupkom su deponovane prevlake  $Al_2O_3$ –40%tež. $TiO_2$  sa tri različite vrednosti plazma struje 700, 800 i 900A. Ispitane su i analizirane mehaničke osobine i mikrostrukture deponovanih prevlaka na osnovu čega se došlo do sledećih zaključaka.

*Mehanička svojstava i mikrostrukture  $Al_2O_3$ -40%tež.  $TiO_2$  prevlaka su bila pod uticajem plazma struje. Veća vrednost plazma struje je povećala mehanička svojstava poboljšala mikrostrukturu i adheziju prevlake.*

*Sa povećanjem plazma struje doponovale su se prevlake sa većim vrednostima mikrotvrdoće i manjim rasponom mikrotvrdoće kroz slojeve prevlaka. Prevlake deponovane sa plazma strujom od 900 A je imala najveće vrednosti mikrotvrdoće i zatezne čvrstoće spoja. Za sve prevlake lom je bio na interfejsu između prevlake i substrata. Vrednosti mikrotvrdoće i zatezne čvrstoće spoja su bile u korelaciji sa njihovim mikrostrukturama.*

*Struktura deponovanih prevlake  $Al_2O_3$ -40%tež.  $TiO_2$  je lamelarna. U prevlakama su prisutne sferne pore crne boje. Najmanji udeo mikro pora od 2% su imali slojevi deponovani sa plazma strujom od 900A, a najveći udeo mikro pora od 6% su imali slojevi deponovani sa plazma strujom od 700A. U strukturi keramičkih prevlaka  $Al_2O_3$ -40%tež.  $TiO_2$  su prisutne dve modifikacije aluminijum oksida  $\alpha$  -  $Al_2O_3$  i  $\gamma$  -  $Al_2O_3$ , titanijum dioksid  $TiO_2$  i dve spinel modifikacije rutila  $\alpha$  -  $Al_2TiO_5$  i  $\beta$  -  $I_2TiO_5$  koje su nastale reakcijom oksida  $Al_2O_3$  i  $TiO_2$  u procesu topljenja praha u plazmi.*

*Prevlake deponovane sa plazma strujom 900A su pokazale najbolje mikrostrukture i mehanička svojstva. Primenom prevlake na vazduhoplovnim delovima oslonaca ležajeva poboljšala se efikasnost delova i pouzdanost rada.*

*Ključne reči: titanijum dioksid; aluminijum oksid; čvrstoća spoja; mikrotvrdoća; interfejs; atmosferski plazma-sprej (APS).*

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