

PROPERTIES OF THE ZrO₂MgO/MgZrO₃NiCr/NiCr TRIPLE- LAYER THERMAL BARRIER COATING DEPOSITED BY THE ATMOSPHERIC PLASMA SPRAY PROCESS

Mihailo R. Mrdak

Research and Development Center IMTEL Communications a.d.,
Belgrade, Republic of Serbia
e-mail: miki@insimtel.com,
ORCID iD: <http://orcid.org/0000-0003-3983-1605>

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Summary:

This paper presents the results of the examinations of TBC - ZrO₂MgO / MgZrO₃NiCr / NiCr thermal barrier layers deposited by the plasma spray process at the atmospheric pressure on substrates of Al alloys. In order to obtain the structural and mechanical properties of layers, which will provide a good heat and abrasion protection of the tail elevators of aircraft J-22 when firing "Lightning" and "Thunder" rockets, the deposition of three powder types was performed on 0.6 mm thick Al alloy substrates. This study describes a procedure of using triple-layer TBC coatings as a good combination among many available ones, which gives a good compromise between thermal protection and resistance to abrasion for protecting aircraft tail elevators. The study is mainly based on the experimental approach. The evaluation of the mechanical properties of layers was done by the examination of microhardness by method HV_{0.3} and bond strength on the tensile machine. The structure of layers was examined by the method of light microscopy while the surface of ZrO₂MgO ceramic layers was examined by the method of scanning electron microscopy (SEM). The thermal protection of TBC layers and resistance to abrasion were tested in the tunnel of the Military Technical Institute, Zarkovo. The obtained characteristics of the surface layers and the rocket firing simulations have proven the triple-layer system of TBC coatings reliable.

Key words: substrates, protective, property, layers, coatings, barriers, alloys.

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Introduction

TBC - thermal barrier plasma spray coatings are widely used to protect parts of turbo jet engines and other engine parts exposed to high temperatures, oxidation, corrosion and erosion of gas particles. Plasma-deposited TBC ceramic coatings are a good solution for the thermal protection of diesel engine parts such as pistons, valves, etc. (Çelik, et al., 1997, pp.361-365), (Demirkiran, Avci, 1999, pp.292-295), (Miyamoto, et al., 1999, p.100). Oxide ZrO_2 was selected because of its high strength and fracture toughness compared to other oxides, and physical characteristics such as a thermal conductivity of $\lambda \approx 1.7$ W/mK, a coefficient of thermal expansion of $\alpha \approx 9 \times 10^{-6}$ 1/K and a melting point of 2710°C (Boutz, et al., 1994, pp.89-102), (Chevalier, et al., 2009, pp.1901-1920). The polymorphism of pure ZrO_2 is an important feature (Johner, Schweitzer, 1984, pp.301-315). At the atmospheric pressure, there are three crystallographic phases: the monoclinic, the tetragonal and the cubic one. When alternating heating and cooling, the thermal fatigue of the ZrO_2 material occurs due to the volume changes caused by the phase transformation. As a result of the reversible transformation of the monoclinic phase into the tetragonal one, the occurrence of microcracks spreading and converting into macro crevices was observed in the temperature range of 950°C-1170°C (Garvie, et al., 1975, pp.703-704), (Garvie, 1970, pp.117-166). For this reason, pure ZrO_2 is not suitable for the preparation of the TBC coating. In order to reduce the effect of the tetragonal transformation into the monoclinic one, other oxides such as MgO, CaO, Y_2O_3 , CeO_2 , HfO_2 , and In_2O_3 are added to pure ZrO_2 . These additives stabilize the ceramic layer partially or in full by forming a cubic structure stable from the room temperature up to more than 2000°C. ZrO_2 with addition of magnesium oxide MgO is often used as a TBC due to its high coefficient of linear expansion that is 11×10^{-6} 1/K, a coefficient of thermal conductivity of 1.5 W/mK, high resistance to thermal cycles, resistance to corrosion, and easy preparation of the coating by plasma spray spraying. When the TBC is subjected to elevated temperatures, this induces mechanical degradation that involves the stratification and cracking of ceramics as a result of the factors such as stresses due to thermal expansion conflicts related to the changes in the microstructure because of thermal cycles. TBC coatings consist of at least two layers. The outer, generally thicker layer is made of a ceramic material or a mixture of ceramics and fire-resistant metals, the primary purpose of which is to provide thermal insulation and resistance to thermal shocks. The material of the ceramic layer which is in a direct contact with the working fluid, has a drop of temperature per cross section even to 400-500°C (Mrdak, et al., 2013, pp.559-567), (Mrdak, et al., 2015, pp.337-343). That

layer should also have resistance to erosive effects and good bonding with the substrate material. The inner, thinner layer provides protection from the oxidative degradation of the base material, but also provides a good bond between the base metal and the outer ceramic layer. In order to reduce stresses, triple-layer systems of TBC coatings are often produced; they consist of the bonding Ni20%Cr layer, the transitional MgZrO₃35%NiCr cermet inter-layer and the top ZrO₂24%MgO ceramic layer. This study describes a method of using the triple-layer TBC coatings as a selection of a good combination among many available options, which provides a good compromise between the thermal protection and the resistance to erosion of the Al alloy substrate for protecting the tail elevators of aircraft J-22. The study is mainly based on the experimental approach. The properties of the deposited materials are generally functions of their microstructures. According to previous studies, plasma deposited ceramic deposits show a lamellar structure with limited inter - lamellar bonding (Li, Ohmori, 2002, pp.365-374) (Mrdak, et al., 2013, pp.559-567). Because of this, micro pores are present in the deposit as volume errors.

This paper presents the examination of a ZrO₂MgO/MgZrO₃NiCr/NiCr triple-layer system of TBC coatings deposited by the atmospheric plasma spraying (APS) process on the substrates of Al alloys, which serve as the thermal abrasive barriers of the tail elevators of aircraft J-22. The aim of the study was to produce the TBC coatings of such structural and mechanical properties of the layers which will provide a good heat and abrasion protection on the aircraft tail elevators when firing "Lightning" and "Thunder" rockets. The microhardness and bond tensile strength of the triple system of TBC coatings and layer microstructures were examined. The obtained characteristics of the TBC layers and rocket firing simulations have proven the triple-layer system of TBC coatings reliable.

Materials and experimental details

The material on which layers of the ZrO₂MgO/MgZrO₃NiCr/NiCr triple-layer TBC coating were deposited was aluminum alloy ENAW-AlMg1(C)(ENAW-5005). For the production of the top ceramic coating layers, the ZrO₂24%MgO powder of the Sulzer Metco company, labelled Metco 210NS-1, was used. The powder is produced by the method of casting into blocks and subsequent grinding of these blocks to obtain a specific granularity. The melting point of powder is 2140°C. The powder with a range of granules of 10-53µm (Metco 210NS-1 Powder Magnesium Zirconate, 2000.Sulzer Metco.Technical Bulletin 10-289) was used for the experiment. Figure 1 shows a (SEM) scanning electron photomicrography of the morphology of ZrO₂24%MgO powder particles. The powder particles are of an irregular angular shape.

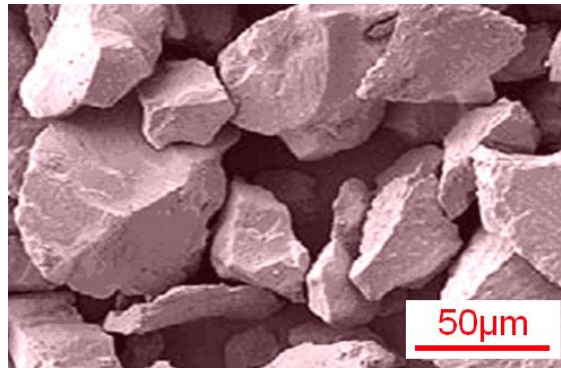


Figure 1 – (SEM) Scanning electron micrography of ZrO_2 24%MgO powder particles
 Slika 1 – (SEM) Skening elektronska mikrografija čestica praha ZrO_2 24%MgO
 Puc. 1 – (SEM) Электронная микрография частиц порошка ZrO_2 24%MgO

For the production of inter-layer TBC coatings, $MgZrO_3$ 35%NiCr cermet powder of the Sulzer Metco company, labelled Metco 303NS – 1, was used. The powder is a mechanical mixture of ZrO_2 MgO powder and NiCr in relation 35%(80Ni20%Cr) + 65%(ZrO_2 24%MgO). Powder with a range of granules of 11-90 μm (Material Product Data Sheet, 2012. Metco 303NS-1 Magnesium Zirconate-Nickel Chromium Cermet Blends. Sulzer Metco DSMTS- 0070.0) was used for the experiment. For the production of the lower bonding layer, the powder type labelled Metco 43F-NS (an alloy of nickel and chromium Ni20%Cr) was used. The melting point of the powder is 1400°C. The powder with a range of granules of 10-63 μm (Material Product Data Sheet, 2012. Metco 43F-NS Nickel-20% Chromium Powders. Sulzer Metco. DSMTS-0109.0) was used for the experiment.

Testing the mechanical properties of the ZrO_2 MgO/ $MgZrO_3$ NiCr/NiCr TBC coating was done according to the Pratt & Whitney standard (Turbojet Engine – Standard Practices Manual (PN 582005), 2002. Pratt & Whitney, East Hartford, USA). The bases with deposited coating layers for the microhardness testing and the evaluation of microstructure in a deposited condition are made of ENAW-AIMg1(C)(ENAW 5005) aluminum alloy with the dimensions 70x20x1.5 mm. The bases for testing bond strength are also made of ENAW-AIMg1(C)(ENAW-5005) aluminum alloy with the dimensions $\varnothing 25 \times 50$ mm. The investigation of the microhardness of the layers was done by the method $HV_{0.3}$ and the bond strength was tested on a tensile machine. Microhardness measurements were performed in the direction along the lamellas. Five readings of microhardness values of the layers were performed in the middle and at the ends of the samples while two extreme values were rejected. Out of three remaining values, minimum and maximum values are shown. The

bond strength testing was done at room temperature with a speed of tensile testing of 1cm/60s. The bond strength testing was performed for each individual coating 43F-NS (80Ni20%Cr), 303NS-1 (MgZrO₃35%NiCr) and 210NS-1 (ZrO₂24%MgO). The bond strength of the ZrO₂MgO/MgZrO₃NiCr/NiCr triple system of TBC coatings was tested as well. Five test pieces were examined for all types of coatings, out of which two extreme values were rejected. The average bond strength value is shown for the three remaining values. The morphology of the ZrO₂24%MgO powder particles and that of the deposited coating surface were determined by using scanning electron microscopy (SEM). The microstructure of the deposited layers was examined on the optical microscope (OM). The analysis of the share of micro pores in the coating layers was done on five photos at the 200X magnification. Over tracing paper, micro pores were labelled and shaded and their total area was counted in relation to the total surface of the micrographs. This paper presents the average value of the shares of micro pores in the TBC coating layers.

The deposition of powders was done with the atmospheric plasma spray system by the Plasmadyne company and the SG-100 plasma gun with controlled plasma spray parameters. The SG-100 plasma gun consisted of the cathode type K 1083A-129, the anode type A 1083-165 and the gas injector type GI 1083-113. Ar as an arched gas was used in combination with He and the power of supply of 40 KW. The plasma spray parameters of the deposition powders are shown in Table 1. Before the depositing process, the surface of the test samples and the surface of the substrate of the thermal abrasive barrier for the aircraft tail elevators were not roughened, due to the small thickness of the substrate of 0.6 mm. The bonding layers were deposited with a thickness of 60-80µm, the cermet layers with a thickness of 40-60µm and the top ceramic layer with a thickness of 280-300µm.

Table – 1 Parameters of the deposition of powders
 Tabela 1 – Parametri depozicije prahova
 Таблица 1 – Параметры напыления порошка

Parameters	43F-NS	303NS-1	210NS-1
Electric Current, I (A)	700	900	900
Arc voltage, U (V)	30	43	43
Primary plasma gas, l/min	50	50	50
Secondary plasma gas, l/min	12	12	12
Carrier gas powder, l/min	7	7	7
Powder feed rate, g/min	50	50	50
Distance of plasma guns, mm	90	100	100



Figure 2 – Section of the edge of the aircraft rear wing with a TBC coating
 Slika 2 – Sekcija ivice zadnjeg krila aviona sa TBC prevlakom
 Рис. 2 – Часть заднего крыла самолета с TBC покрытием

Figure 2 shows one section of the edge of the aircraft tail elevators with a deposited TBC coating.

Results and discussion

The values of microhardness and bond strength of TBC coating systems are shown in Figures 3 and 4. The metal bonding coating 43F-NS (Ni20%Cr) had the lowest values of microhardness of 238-254HV_{0.3}, which are within the limits of values prescribed by the powder manufacturer and by the standard (Material Product Data Sheet, 2012. Metco 43F-NS Nickel-20% Chromium Powders, Sulzer Metco. DSMTS-0109.0) (Turbojet Engine-Standard Practices Manual (PN 582005) 2002. Pratt & Whitney, East Hartford, USA). The measured values of the microhardness of the bonding layers indicate that the share of micro pores is within the prescribed limits, which was confirmed by the analysis of the shares of micro pores. Due to ceramics content, the layers of the cermet coating 303NS-1 (MgZrO₃35%NiCr) had higher values of microhardness, in a range of 293-330HV_{0.3} and in accordance with the Pratt & Whitney standard (Turbojet Engine-Standard Practices Manual (PN 582005) 2002. Pratt & Whitney, East Hartford, USA).

The layers of the ceramic coating Metco 210NS-1 (ZrO₂24%MgO) had the highest microhardness values of 478-519HV_{0.3} that are characteristic for this type of the coating. These layers had the highest share of micro pores because ceramic particles create a weaker inter-lamellar contact in comparison to metal particles. Figure 3 shows the minimum and maximum values of the microhardness of TBC coatings.

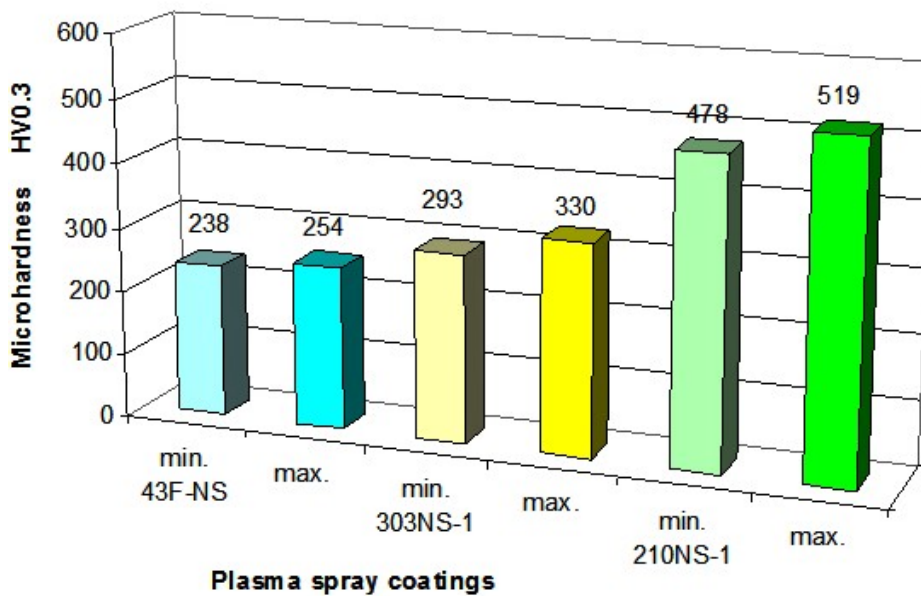


Figure 3 – Microhardness of ZrO₂24%MgO, MgZrO₃ 35%NiCr and Ni20%Cr coatings
 Slika 3 – Mikrotvrdoća ZrO₂24%MgO, MgZrO₃ 35%NiCr i Ni20%Cr prevlaka
 Рис. 3 – Микротвердость ZrO₂24%MgO, MgZrO₃ 35%NiCr i Ni20%Cr покрытия

The tensile bond strength of coatings was directly related to the powder type. The highest bond strength values of 31 MPa were found in the metal bonding layers of 43F-NS(Ni20%Cr) coating. The layers of cermet coating 303NS-1 (MgZrO₃35%NiCr) had a tensile bond strength of 22 MPa, while a minimum value of 17 MPa was found in the ceramic layers of Metco 210NS-1 (ZrO₂24%MgO). For all coatings, the bond strength values were good because the coatings were deposited on the non-roughened substrates of Al alloy which reduce the tensile bond strength in relation to roughened substrates based on Fe or Ni alloys.

The average tensile strength value of the ZrO₂MgO/MgZrO₃NiCr/NiCr system of TBC coatings was 30 MPa. The TBC coating was destroyed at the substrate/coating interface, which was expected due to two different materials. The measured values of microhardness and tensile bond

strength of the $ZrO_2MgO/MgZrO_3NiCr/NiCr$ system of of TBC coatings were in correlation with the microstructure of deposited layers.

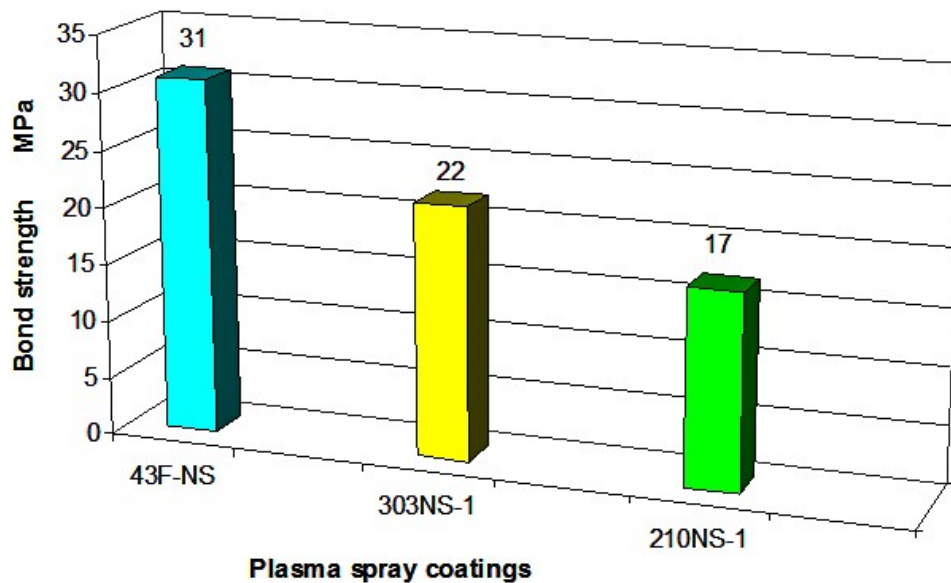


Figure 4 – Bond strength of $ZrO_224%MgO$, $MgZrO_335%NiCr$ and $Ni20%Cr$ coatings
 Slika 4 – Čvrstoća spoja $ZrO_224%MgO$, $MgZrO_335%NiCr$ and $Ni20%Cr$ prevlaka
 Рис. 4 – Микропрочность соединений $ZrO_224%MgO$, $MgZrO_335%NiCr$ and $Ni20%Cr$ покрытия

Figures 5 and 6 shows the microstructure of the triple system of thermal barrier coatings TBC – $ZrO_224%MgO/MgZrO_335%NiCr/Ni20%Cr$. The photomicrographs clearly show the boundaries of the interface between the bonding coating layers and the substrate, the bonding coating and the cermet coatings, as well as between the cermet coatings and the ceramic coatings. The interface between the substrate and the bonding coating layers is very clean, which indicates a good bond between the coating layers with the substrate. At the interface between the substrate and the bonding coating layers there are no defects such as discontinuities of deposited layers, microcracks, macrocracks, coating peeling and separation from the substrate. Generally, the layers are uniformly deposited on the substrate. Along the following interfaces: the substrate / the bonding coatings, the bonding coatings / the cermet coatings and the cermet coatings / the ceramic coatings, there are no microcracks and macrocracks present. The bond between all layers is good.

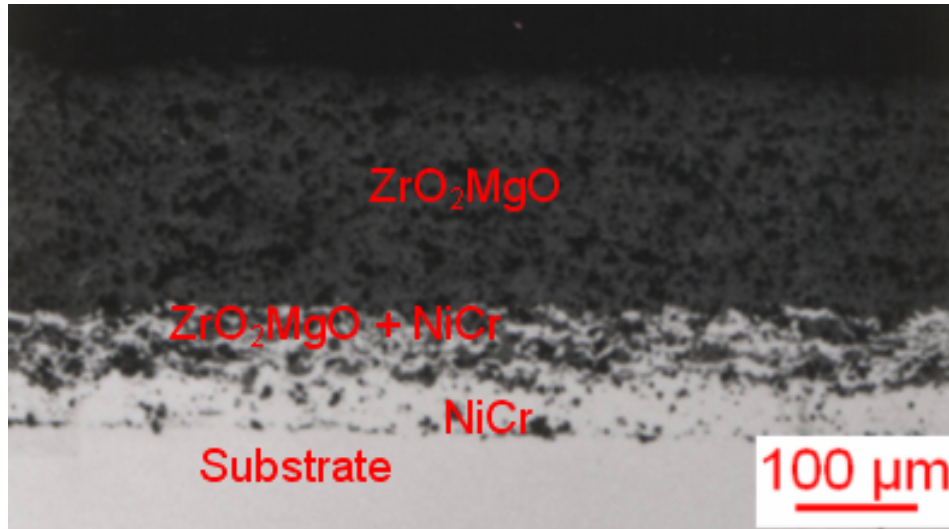


Figure 5 – Microstructure of the triple layer of $ZrO_2MgO/MgZrO_3NiCr/NiCr$ coatings
 Slika 5 – Mikrotvrdoća troslojne prevlake $ZrO_2MgO/MgZrO_3NiCr/NiCr$
 Рус. 5 – Микротвердость трехслойного покрытия $ZrO_2MgO/MgZrO_3NiCr/NiCr$

In the layers of deposited coatings, there were no unmelted powder particles observed, which indicates that the powders were deposited with the optimal deposition parameters. The analysis of the photomicrographs showed that in the layers of bonding coatings 43F-NS (Ni20%Cr) there were micro pores with an average share of 2.6%. The share of micro pores in the layers of cermet coatings 303NS-1 ($MgZrO_3$ 35%NiCr) was 7%, and the layers of ceramic coatings 210NS-1 (ZrO_2 24%MgO) had the content of micro pores of 12%.

The microstructure of the Ni20%Cr bonding coating is lamellar. The coating base is a solid solution of chromium in nickel γ - Ni(Cr). Between the lamellas of the solid solution in the coating layers there are light gray oxides: NiO, $NiCr_2O_4$, Cr_2O_3 and CrO_3 (Nicoll, 1984), (Mrdak, 2015, pp.32-55) due to oxidation of powder particles in plasma during the process of coating formation. In most cases, the oxide of chromium Cr_2O_3 is present and, in rare cases, oxide CrO_3 , formed in a thin layer on the surface of NiCr lamellae (Brossard, et al., 2010, pp.1608-1615). In the middle cermet inter-layer, there are clearly visible light gray lamellae of the bonding coating, evenly distributed between ceramic lamellae in dark gray. The top ceramic layer is uniformly deposited on the cermet layer in which black micro pores can be seen.

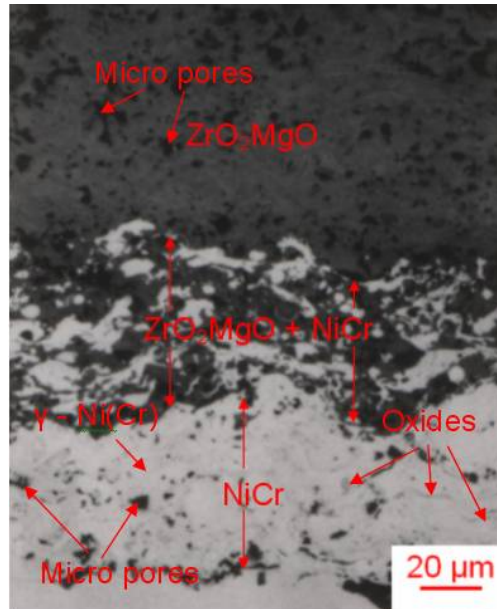


Figure 6 – Microstructure of the triple layer of $ZrO_2MgO/MgZrO_3NiCr/NiCr$ coatings
 Slika 6 – Mikrotvrdoća troslojne prevlake $ZrO_2MgO/MgZrO_3NiCr/NiCr$
 Рус. 6 – Микротвердость трехслойного покрытия $ZrO_2MgO/MgZrO_3NiCr/NiCr$

Figure 7 shows a SEM photomicrograph of the surface of a ZrO_2MgO molten particle. The SEM analysis of the morphology of the surface of the deposited ceramic ZrO_2MgO powder particle shows a complete melting and casting of ceramic particles on the previously deposited ceramic layer.

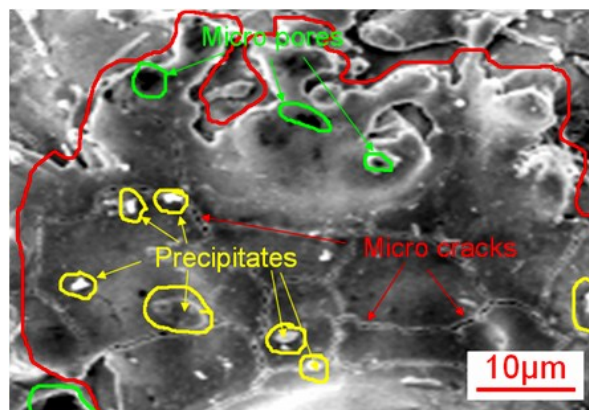


Figure 7 – (SEM) Morphology of the ZrO_2MgO coating surface
 Slika 7 – (SEM) Morfologija površine ZrO_2MgO prevlake
 Рус. 7 – Морфология поверхности ZrO_2MgO покрытия

The surface of the molten ZrO₂MgO powder particle was circled with a red line on the SEM micrograph. The molten powder particle formed an almost circular shape in the collision with the surface of the previously deposited layer. The surface of the particle shows a fine net of microcracks which cannot be avoided and which always occurs in the deposition process (Guo, et al., 2011, pp.161-174).

Microcracks are formed during the cooling of molten particles to the coating temperature. The inner coating layers, which have a higher temperature compared to that of the coating surface, are exposed to tensile stress and are opposed to the shrinkage of the particles on the coating surface. On the other hand, the particles on the coating surface while cooling and shrinking during solidification, are exposed to compression stresses. Microcracks on the particle surface are caused by tensile stresses of deposited layers which are always higher than compression stresses of the particles while cooling Guo, et al., 2011, pp.161-174), (Mrdak, et al. 2013, pp.559-567), (Mrdak, 2013, pp.426-432), (Mrdak, et al., 2015, pp.337-343). In the microstructure, there are fine precipitates of irregular shapes with a size up to 5 μm, circled in yellow. On the SEM micrograph, micro pores of irregular shapes in black with a size up to 5 μm are clearly seen and circled in green.

Conclusion

This paper describes how the APS - atmospheric plasma spray process was used to produce a triple-layer system of thermal barrier coatings TBC - ZrO₂24%MgO/MgZrO₃35%NiCr/Ni20%Cr. The system of the deposited coatings consisted of the Ni80%Cr bonding layer, the intermediary MgZrO₃35%NiCr inter-cermet layer and the top ZrO₂24%MgO ceramic layer. The coatings were deposited on the test Al alloy samples on the surfaces without roughening. The mechanical properties and the microstructures of the coating layers were analyzed in the deposited condition, which led to the following conclusions.

The triple-layer system of the thermal barrier coatings had good mechanical properties with the bonding layer microhardness values of 238-254HV_{0.3}, the intermediary cermet layer microhardness values of 293-330HV_{0.3} and the top ceramic layer microhardness values of 478-519HV_{0.3}. The microhardness values were within the limits prescribed by the Pratt&Whitney standard. The bond strength of the deposited coatings on the non-roughened Al alloy samples had good values. The tensile bond strength was 31 MPa for the bonding layer, 22 MPa for the cermet coating and 17 MPa for the ceramics. The bond strength of the triple-layer system of TBC coatings is 30 MPa. The analysis of the photomicrographs has shown that the average share of micro pores was 2.6% in the bonding

layers, 7% in the cermet layers and 12% in the ceramic layers. The microstructure of the deposited coating layers is lamellar.

The coating base consists of a solid solution of chromium in nickel γ - Ni(Cr). There are light gray NiO, NiCr₂O₄, Cr₂O₃ and CrO₃ oxides between the solid solution lamellae in the coating layers due to oxidation of powder particles in plasma during the coating formation process. In most cases, the oxide of chromium Cr₂O₃ is present and, in rare cases, oxide CrO₃, formed in a thin layer on the surface of NiCr lamellae. The cermet inter-layer had a uniform distribution of bond coating lamellae between ceramic lamellae. The top ceramic layer is uniformly deposited on the cermet layer without the presence of unmelted particles.

The triple-layer system of thermal barrier coatings - ZrO₂24%MgO / MgZrO₃35%NiCr / Ni20%Cr, deposited on the Al alloy substrate as the thermal abrasive protection of the tail elevators of aircraft J-22, proved to be reliable protection against the jet temperature and jet abrasive particles during firing of "Lightning" and "Thunder" rockets.

Literature

Boutz, M.M.R., Winnubst, A.J.A., Burggraaf, A.J., 1994, Yttria-ceria stabilized tetragonal zirconia polycrystals: Sintering, grain growth and grain boundary segregation, *Journal of the European Ceramic Society*, 13(2), pp.89-102.

Brossard, S., Munroe, P.R., Tran, A.T.T., Hyland, M.M., 2010, Study of the microstructure of NiCr splats plasma sprayed on to stainless steel substrates by TEM, *Surface and Coatings Technology*, 204(9-10), pp.1608-1615.

Celik E, Avci E, Yilmaz F., 1997, Evaluation of Interface Reactions in Thermal Barrier Ceramic Coatings, *Surf. Coatings Technol.*, 97, pp.361-365.

Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009, The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends, *Journal of the American Ceramic Society*, 92(9), pp.1901-1920.

Demirkiran, A.S., Avci, E., 1999, Evaluation of functionally gradient coatings produced by plasma-spray technique. *Surf. Coat. Technol.* 116-119, pp.292-295.

Garvie, R.C., 1970, Zirconium dioxide and some of its binary systems, in: Alper, A.M., (ed.), *High-temperature oxides*, Vol. 5-II, Academic Press, New York, pp.117-166.

Garvie, R.C., Hannink, R.H.J., and Pascoe, R.T., 1975, 'Ceramic steel?', *Nature*, 258, pp.703-704.

Guo, H., Yao, R. and Zhpu, L., 2011, in 'Thermal barrier coatings', (ed. Xu, H. and Guo, H.) Cambridge, Woodhead Publishing Limited, pp.161-174.

Johner, G., Schweitzer, K.K., 1984, Thermal barrier coatings for jet engine improvement, *Thin Solid Films*, 119(3), pp.301-315.

Li, C.-J. and Ohmori, A., 2002, Relationships Between the Microstructure and Properties of Thermally Sprayed Deposits, *J. Thermal Spray Technol.*, 11(3), pp.365-374.

Material Product Data Sheet, 2012, Metco 43F-NS Nickel - 20% Chromium Powders. Sulzer Metco. DSMTS-0109.0.

Material Product Data Sheet, 2012, Metco 303NS-1 Magnesium Zirconate - Nickel Chromium Cermet Blends. Sulzer Metco. DSMTS-0070.0.

Metco 210NS-1 Magnesium Zirconate Powder, 2000, Sulzer Metco. Technical bulletin 10-289.

Miyamoto, Y., Kaysser, W.A., Rabin, B.H., Kawasaki, A., Ford, R.G., 1999, Functionally Graded Materials: Design, Processing and Applications, Kluwer Academic Publisher, Boston, p.100.

Mrdak, M., 2013, Ispitivanje mehaničkih i strukturnih osobina prevlaka otpornih na eroziju i visoke temperature, pp.426-432, SERBIATRIB '13, 13th International Conference on Tribology, Serbia, Kragujevac, 15-17.

Mrdak, M., Vencl, A., Nedeljkovic, B., Stanković, M., 2013, Influence of plasma spraying parameters on properties of the thermal barrier coatings, Materials Science and Technology, 29(5), pp.559-567.

Mrdak, M., Rakin, M., Medjo, B., Bajić, N., 2015, Experimental Study of Insulating Properties and Behaviour of Thermal Barrier Coating Systems in Thermo Cyclic Conditions, Materials & Design, 67, pp.337-343.

Mrdak, M., 2015, Investigation of the influence of plasma spray sealing coatings on the effect of sealing the TV2-117A turbojet engine compressor, *Vojnotehnički glasnik/Military Technical Courier*, 63(1), pp.32-55.

Nicoll, A.R., 1984, The environment – high temperature oxidation and hot corrosion, u: CEI Course on High Temperature Materials and Coatings, Finland.

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

ХАРАКТЕРИСТИКИ ТРЕХСЛОЙНЫХ ТЕРМОБАРЬЕРНЫХ ПОКРЫТИЙ $ZrO_2MgO/MgZrO_3NiCr/NiCr$, НАНЕСЕННЫХ ВОЗДУШНО-ПЛАЗМЕННЫМ НАПЫЛЕНИЕМ

Михаило Р. Мрдак
Центр исследований и развития А.О. «ИМТЕЛ коммуникации», Белград,
Республика Сербия

ОБЛАСТЬ: химические технологии
ВИД СТАТЬИ: оригинальная научная статья
ЯЗЫК СТАТЬИ: английский

Резюме:

В данной статье представлены результаты испытаний термобарьерных покрытий ТБС $ZrO_2MgO/MgZrO_3NiCr/NiCr$, нанесенных воздушно-плазменным напылением при атмосферном давлении на субстраты сплавов Al.

Испытания проводились с целью получения структурных и механических характеристик слоев, обеспечивающих качественную и абразивную защиту задних крыльев самолета J-22 при выпуске ракет, а также от грома и молний. Нанесено напыление трех типов порошков на субстраты сплавов Al, толщиной 0,6мм.

В данном исследовании представлен метод применения трехслойного ТБС покрытия, которое обладает лучшими защитными свойствами, когда речь идет о термоизоляции и защите от абразивного износа задних крыльев самолета.

Анализ механических характеристик покрытия проведен на основании испытаний микротвердости методом $HV_{0.3}$ и прочности соединений методом растяжения. Структура слоев испытана методом оптической микроскопии, а поверхность ZrO_2MgO испытана методом электронной микрографии (SEM).

Испытания теплоизоляционных ТБС слоев и сопротивления абразивному износу были проведены в аэродинамической трубе Военно-технического института Жарково. На основании полученных характеристик поверхности слоев и моделирования выпуска ракет, можно утверждать, что трехслойные системы ТБС являются надежным способом покрытия.

Ключевые слова: субстраты, защита, характеристика, слою, покрытие, барьер, сплавы.

SVOJSTVA TROSLOJNE TERMOBARIJERNE PREVLAKE $ZrO_2MgO/MgZrO_3NiCr/NiCr$ DEPONOVA NE ATMOSFERSKIM PLAZMA SPREJ PROCESOM

Mihailo R. Mrdak

Istraživački i razvojni centar IMTEL Komunikacije a. d., Beograd,
Republika Srbija

OBLAST: hemijske tehnologije

VRSTA ČLANKA: originalni naučni članak

JEZIK ČLANKA: engleski

Sažetak:

U radu su prikazani rezultati ispitivanja termobarijernih slojeva TBC – $ZrO_2MgO/MgZrO_3NiCr/NiCr$ koji su deponovani plazma sprej procesom na atmosferskom pritisku na substratima od legure Al. Radi dobijanja strukturnih i mehaničkih osobina slojeva, koji će obezbediti dobru toplotnu i abrazivnu zaštitu zadnjim krilima aviona J-22 pri ispaljivanju raketa munje i groma, izvršena je depozicija tri tipa praha na substratima od legure Al debljine 0,6 mm. Ova studija opisuje postupak korišćenja troslojne TBC prevlake kao izbor dobre kombinacije od mnogo raspoloživih mogućnosti, koja predstavlja kompromis između toplotne zaštite i otpornosti na abraziju za zaštitu zadnjih krila aviona. Studija se, uglavnom, zasniva na eksperimentalnom pristupu. Procena mehaničkih osobina slojeva urađena je ispitivanjem mikrotvrdoće me-

tođom $HV_{0.3}$ i đvrstoće spoja ispitivanjem na zatezanje. Struktura slojeva ispitana je metodom svetlosne mikroskopije i površina ZrO_2MgO keramičkih slojeva metodom skenirajuće elektronske mikroskopije (SEM). Toplotna zaštita TBC slojeva i otpornost na abraziju ispitana je u tunelu Vojnotehničkog instituta iz Źarkova. Na osnovu dobijenih karakteristika površinskih slojeva i simuliranja ispaljivanja rakete, troslojni sistem TBC prevlake pokazao se pouzđanim.

Uvod

TBC termobarijerne plazma sprej prevlake uveliko se koriste kao zaštita delova turbomlaznih motora i za druge delove motora izlođene visokim temperaturama, oksidaciji, gasnoj koroziji i eroziji čestica. Plazmom deponovane TBC keramičke prevlake dobro su rešenje za toplotnu zaštitu delova dizel motora, kao što su klipovi, ventili, itd. (Đelik, et al., 1997, pp.361-365), (Demirkiran, Avci, 1999, pp.292-295), (Miyamoto, et al., 1999, p.100). Izbor oksida ZrO_2 izvršen je zbog visoke đvrstoće i Źilavosti loma u odnosu na druge okside i fizičkih karakteristika, kao što je toplotna provodljivost $\lambda \approx 1.7$ W/mK, koeficijent termičke ekspanzije $\alpha \approx 9 \times 10^{-6}$ 1/K i temperature topljenja 2710°C (Boutz, et al., 1994, pp.89-102), (Chevalier, et al., 2009, pp.1901-1920). Na atmosferskom pritisku postoje tri kristalografske faze: monoklinična, tetragonalna i kubna. Prilikom naizmeničnog zagrevanja i hlađenja dolazi do toplotnog zamora ZrO_2 materijala usled zapreminskih promena uzrokovanih faznom transformacijom. Kao posledica reverzibilne transformacije monoklinične faze u tetragonalnu u temperaturnom opsegu od 950° do 1170°C uočen je nastanak mikropukotina koje se šire i pretvaraju u makropukotine (Garvie, et al., 1975, pp.703-704), (Garvie, 1970, pp.117-166). Zbog toga čisti ZrO_2 nije pogodan za izradu TBC prevlaka. Radi smanjenja efekta tetragonalne transformacije u monokliničnu, čistom ZrO_2 dodaju se drugi oksidi, kao što su: MgO , CaO , Y_2O_3 , CeO_2 , HfO_2 i In_2O_3 . ZrO_2 sa dodatkom magnezijumoksida MgO često se koristi kao TBC zbog velikog koeficijenta linearnog širenja koji je 11×10^{-6} 1/K, koeficijenta toplotne provodljivosti 1,5 W/mK, velike otpornosti na toplotne cikluse, otpornosti na koroziju i lake izrade prevlake plazma sprej prskanjem. TBC prevlake sastoje se najmanje od dva sloja: spoljašnjeg, po pravilu debljeg sloja, sačinjenog od keramičkog materijala ili mešavine keramike i vatropostojanih metala, koji pre svega treba da obezbedi toplotnu izolaciju i otpornost na termošokove. Materijal keramičkog sloja koji se nalazi u direktnom kontaktu sa radnim fluidom ima pad temperature po preseku i do $400\text{--}500^\circ\text{C}$ (Mrdak, et al., 2013, pp.559-567), (Mrdak, et al., 2015, pp.337-343). Da bi se smanjili naponi često se proizvode troslojni sistemi TBC prevlaka koji se sastoje od veznog sloja $Ni20\%Cr$, prelaznog kermet međusloja $MgZrO_335\%NiCr$ i gornjeg keramičkog sloja $ZrO_224\%MgO$. Ova studija

opisuje postupak korišćenja troslojne TBC prevlake kao izbor dobre kombinacije, od mnogo raspoloživih mogućnosti, koja daje dobar kompromis između toplotne zaštite i otpornosti na eroziju substrata od legure Al za zaštitu zadnjih krila aviona J-22. Studija se uglavnom zasnivala na eksperimentalnom pristupu. Svojstva deponovanih materijala su generalno funkcije njihovih mikrostruktura.

U ovom radu ispitan je troslojni sistem TBC prevlaka $ZrO_2MgO/MgZrO_3NiCr/NiCr$ koji je deponovan atmosferskim plazma sprej (APS) postupkom na substratima od legure Al, koji služe kao termoabrazivna barijera zadnjim krilima aviona J-22. Cilj rada je bio da se proizvedu TBC prevlake strukturnih i mehaničkih osobina slojeva, koji će obezbediti dobru toplotnu i abrazivnu zaštitu zadnjim krilima aviona pri ispaljivanju raketa munje i groma. Ispitane su mikrotvrdoće i zatezne čvrstoće spoja trojnih sistema TBC prevlaka i mikrostrukture slojeva. Na osnovu dobijenih karakteristika TBC slojeva i simuliranja ispaljivanja rakete troslojni sistem TBC prevlake pokazao se pouzdanim.

Materijali i eksperimentalni detalji

Materijal na kojem su deponovani slojevi troslojne TBC – $ZrO_2MgO/MgZrO_3NiCr/NiCr$ prevlake bio je od legure aluminijuma ENAW- $AlMg1(C)$ (ENAW-5005A). Za izradu slojeva gornje keramičke prevlake upotrebljen je prah $ZrO_224%MgO$ firme Sulzer Metco sa oznakom Metco 210NS-1. Prah je proizveden metodom livenja u blokove i naknadnim mlevenjem blokova na određenu granulaciju. Temperatura topljenja praha je $2140^{\circ}C$. Za eksperiment se koristio prah koji je imao raspon granulata od 10 do $53\mu m$, a čestice praha su nepravilnog uglastog oblika (Metco 210NS-1 Magnesium Zirconate Powder, 2000. Sulzer Metco. Technical bulletin 10-289). Za izradu srednjih slojeva TBC prevlake upotrebljen je kermet prah $MgZrO_335%NiCr$, firme Sulzer Metco, koji nosi oznaku Metco 303 NS-1. Prah je mehanička mešavina praha ZrO_2MgO i NiCr u odnosu $35\%(80Ni20%Cr)+65\%(ZrO_224%MgO)$. Za eksperiment se koristio prah koji je imao raspon granulata od 11 do $90\mu m$ (Material Product Data Sheet, 2012. Metco 303NS-1 Magnesium Zirconate – Nickel Chromium Cermet Blends. Sulzer Metco. DSMTS-0070.0). Za izradu donjeg veznog sloja koristio se prah oznake Metco 43F-NS, koji je legura nikla i hroma $Ni20%Cr$. Temperatura topljenja praha je $1400^{\circ}C$. Za eksperiment se koristio prah koji je imao raspon granulata od 10 do $63\mu m$ (Material Product Data Sheet, 2012. Metco 43F-NS Nickel - 20% Chromium Powders, Sulzer Metco. DSMTS-0109.0).

Ispitivanje mehaničkih karakteristika slojeva TBC prevlake $ZrO_2MgO/MgZrO_3NiCr/NiCr$ rađeno je prema standardu Pratt & Whitney (Turbojet Engine – Standard Practices Manual (PN 582005), 2002. Pratt & Whitney, East Hartford, USA). Osnove na kojima su deponova-

ni slojevi prevlake za ispitivanje mikrotvrdoće i za procenu mikrostrukture u deponovanom stanju izrađene su od legure aluminijuma ENAW- AlMg1(C) (ENAW-5005A) dimenzija 70x20x1,5 mm. Osnove za ispitivanje čvrstoće spoja takođe su izrađene od legure aluminijuma ENAW- AlMg1(C) (ENAW-5005A), dimenzija $\text{Ø}25 \times 50$ mm. Ispitivanje mikrotvrdoće slojeva rađeno je metodom $\text{HV}_{0,3}$ i čvrstoće spoja ispitivanjem na zatezanje. Merenje mikrotvrdoće izvršeno je u pravcu duž lamela. Izvršeno je pet očitavanja vrednosti mikrotvrdoće slojeva u sredini i na krajevima uzoraka od kojih su odbačene dve krajnje vrednosti. Od tri preostale vrednosti prikazane su minimalne i maksimalne vrednosti. Ispitivanje čvrstoće spoja rađeno je na sobnoj temperaturi sa brzinom zatezanja 1cm/60s. Izvršeno je ispitivanje čvrstoće spoja pojedinačno svake prevlake 43F-NS(80Ni20%Cr), 303NS-1(MgZrO₃35%NiCr) i 210NS-(ZrO₂24%MgO), kao i ispitivanje čvrstoće spoja trojnog sistema TBC – ZrO₂MgO/MgZrO₃NiCr/NiCr prevlaka. Ispitano je po pet epruveta za sve tipove prevlaka od kojih su odbačene dve krajnje vrednosti. Od tri preostale vrednosti prikazana je srednja vrednost čvrstoće spoja. Morfologija čestica praha ZrO₂24%MgO i površina deponovane prevlake urađena je skening elektronskom mikroskopijom (SEM). Mikrostruktura deponovanih slojeva ispitana je na optičkom mikroskopu (OM). Analiza udela mikropora u slojevima prevlake urađena je obradom 5 fotografija na uveličanju 200x. Preko paus papira mikropore su označene i osenčene, a njihova ukupna površina računala se na ukupnu površinu mikrofotografije. U radu je prikazana srednja vrednost udela mikropora u slojevima TBC prevlake.

Depozicija prahova urađena je sa atmosferski plazma sprej sistemom, firme Plasmadyne, i plazma pištoljem SG-100, sa kontrolisanim plazma sprej parametrima. Plazma pištolj SG-100 sastojao se od katode tipa K 1083A-129, anode tipa A 1083-165 i gas injektora tipa GI 1083A-113. Kao lučni gas koristio se Ar u kombinaciji sa He i snaga napajanja do 40 KW. Pre procesa deponovanja površine ispitnih uzoraka i površina substrata termoabrazivne barijere za zadnja krila aviona nisu hrapavljene, zbog male debljine substrata od 0,6mm. Vezni slojevi su deponovani sa debljinom od 60 do 80 μm , kermet slojevi sa debljinom od 40 do 60 μm i gornji keramički sloj sa debljinom od 280 do 300 μm .

Rezultati i diskusija

Vezna metalna prevlaka 43F-NS(Ni20%Cr) imala je najmanje vrednosti mikrotvrdoće od 238 do 254 $\text{HV}_{0,3}$, koje su u granicama vrednosti koje propisuje proizvođač praha i standard (Material Product Data Sheet, 2012. Metco 43F-NS Nickel - 20% Chromium Powders. Sulzer Metco. DSMTS-0109.0), (Turbojet Engine-Standard Practices Manual (PN 582005) 2002. Pratt & Whitney, East Hartford, USA). Izmerene

vrednosti mikrotvrdoće veznih slojeva ukazuju na to da je udeo mikropora u propisanim granicama, što je potvrdila analiza udela mikropora. Zbog sadržaja keramike slojevi kermet prevlake 303NS-1(MgZrO₃35%NiCr) imali su veće vrednosti mikrotvrdoće, koje su bile u rasponu 293-330HV_{0,3} i u skladu sa standardom Pratt & Whitney (Turbojet Engine – Standard Practices Manual (PN 582005)(2002), Pratt & Whitney, East Hartford, USA). Slojevi keramičke prevlake Metco 210NS-1(ZrO₂24%MgO) imali su najveće vrednosti mikrotvrdoće od 478 do 519HV_{0,3} koje su karakteristične za ovaj tip prevlake. Ovi slojevi su pokazali najveći udeo mikropora, jer keramičke čestice ostvaruju slabiji međulamelarni kontakt u odnosu na metalne čestice. Zatezna čvrstoća spoja prevlaka bila je u direktnoj vezi sa tipom praha. Najveće vrenosti čvrstoće spoja od 31 MPa imali su metalni vezni slojevi prevlake 43F- NS (Ni20%Cr). Slojevi kermet prevlake 303NS-1(MgZrO₃35%NiCr) imali su zateznu čvrstoću spoja od 22 MPa, a najmanju vrednost od 17 MPa imali su keramički slojevi Metco 210NS-1 (ZrO₂24%MgO). Za sve prevlake vrednosti čvrstoće spoja bile su dobre, jer su se prevlake deponovale na neohrapavljenim substratima od legure Al koji umanjuju zateznu čvrstoću spoja u odnosu na hrapavljene substrate na bazi legura Fe ili Ni. Srednja vrednost zatezne čvrstoće sistema TBC – ZrO₂MgO/MgZrO₃NiCr/NiCr prevlaka bila je 30 MPa.

Na uzorcima se jasno uočavaju granice međuspoja između slojeva vezne prevlake i substrata, vezne prevlake i kermet prevlake i kermet prevlake i keramičke prevlake. Međugranica između substrata i slojeva vezne prevlake je izuzetno čista, ukazujući na dobru vezu slojeva prevlake sa substratom. Na interfejsu između substrata i slojeva vezne prevlake nisu prisutni defekti kao što je diskontinuitet deponovanih slojeva, mikropukotine, makropukotine, ljuštenje i odvajanje prevlake sa substrata. Generalno, slojevi su ravnomerno deponovani na podlogu. Duž interfejsa između substrata/vezna prevlaka, vezna prevlaka/kermet prevlaka i kermet prevlaka/keramička prevlaka nisu prisutne mikropukotine i makropukotine. Veza između svih slojeva je dobra. U slojevima deponovanih prevlaka nisu uočene neistopljene čestice praha, ukazujući da su prahovi deponovani sa optimalnim parametrima depozicije. Analiza mikrofotografija je pokazala da su u slojevima vezne prevlake 43F-NS(Ni20%Cr) prisutne mikropore sa srednjim udelom od 2,6%. Udeo mikropora u slojevima kermet prevlake 303NS-1(MgZrO₃35%NiCr) bio je 7%, a u slojevima keramičke prevlake 210NS-1 (ZrO₂24%MgO); sadržaj mikropora bio je 12%. Analiza mikrofotografija je pokazala da su u slojevima vezne prevlake 43F-NS(Ni20%Cr) prisutne mikropore sa srednjim udelom od 2,6%. Udeo mikropora u slojevima kermet prevlake 303NS-1(MgZrO₃35%NiCr) bio je 7%, a u slojevima keramičke prevlake 210NS-1 (ZrO₂24%MgO) sadržaj mikropora iznosio je 12%. SEM analiza morfologije površine deponovane keramičke čestice praha ZrO₂MgO pokazuje potpuno toplje-

nje i razlivanje keramičkih čestica na prethodno deponovani keramički sloj. Istopljena čestica praha je u sudaru sa površinom prethodno deponovanog sloja formirala približno kružan oblik. Na površini čestice vidi se fina mreža mikropukotina koja se ne može izbeći i uvek se javlja u procesu depozicije (Guo, et al., 2011, pp.161-174). Mikropukotine se formiraju za vreme hlađenja istopljene čestice do temperature prevlake. Unutrašnji slojevi prevlake koji imaju veću temperaturu u odnosu na površinu prevlake izloženi su naponima na istezanje i suprotstavljaju se skupljanju čestice na površini prevlake. S druge strane, čestica na površini prevlake koja se hladi i skuplja tokom očvršćavanja izložena je naponima na sabijanje. Naponi na istezanje deponovanih slojeva koji su uvek veći od napona na sabijanje čestice koja se hladi na površini prevlake uzrokuju stvaranje mikropukotina na površini čestice (Guo, et al., 2011, pp.161–174), (Mrdak, et al. 2013b, pp.559-567), (Mrdak, 2013a, pp.426-432), (Mrdak, et al., 2015a, pp.337-343). U mikrostrukturi su prisutni fini precipitati nepravilnog oblika veličine do 5 μm , koji su zaokruženi žutom bojom. Na SEM mikrofotografiji jasno se vide mikropore nepravilnog oblika crne boje, veličine do 5 μm , zaokružene zelenom bojom.

Zaključak

U ovom radu je atmosferskim plazma sprej procesom (APS) proizveden troslojni sistem termobarijernih prevlaka TBC-ZrO₂24%MgO/MgZrO₃35%NiCr/ Ni20%Cr. Sistem deponovanih prevlaka sastojao se od veznog sloja Ni80%Cr, srednjeg prelaznog međukermet sloja MgZrO₃35%NiCr i gornjeg keramičkog sloja ZrO₂ 24%MgO. Prevlake su deponovane na ispitnim uzorcima od legure Al na površinama bez hrapavljenja. Analizirane su mehaničke karakteristike i mikrostrukture slojeva prevlaka u deponovanom stanju, na osnovu čega se došlo do određenih zaključaka.

Troslojni sistem termobarijernih prevlaka imao je dobre mehaničke karakteristike sa vrednostima mikrotvrdoće veznog sloja od 238 do 254HV_{0.3}, prelaznog kermet sloja od 293 do 330HV_{0.3} i gornjeg keramičkog sloja od 478 do 519HV_{0.3}. Vrednosti mikrotvrdoće bile su u granicama koje propisuje standard Pratt & Whitney. Čvrstoće spoja deponovanih prevlaka na neohrapavljenim uzorcima od legure Al imale su dobre vrednosti. Za vezni sloj zatezna čvrstoća spoja bila je 31 MPa, za kermet prevlaku 22 MPa, a za keramiku 17 MPa. Čvrstoća spoja troslojnog sistema TBC prevlaka bila je 30 MPa. Analiza mikrofotografija je pokazala da je srednji udeo mikropora u veznim slojevima bio 2,6%, u kermet slojevima 7% i u keramičkim 12%. Mikrostruktura deponovanih slojeva prevlaka je lamelarna. Osnova prevlake sastoji se od čvrstog rastvora hroma u niklu γ – Ni(Cr). Između lamela čvrstog rastvora u slojevima prevlake prisutni su svetlosivi oksidi tipa NiO, Ni-

Cr_2O_4 , Cr_2O_3 i CrO_3 , usled oksidacije čestica praha u plazmi tokom procesa izrade prevlake. U većini slučajeva prisutan je oksid hroma Cr_2O_3 , a ređe oksid CrO_3 , koji se formiraju u vidu tankog sloja na površini NiCr lamela. Kermet međusloj imao je ravnomernu raspodelu lamela vezne prevlake između keramičkih lamela. Gornji keramički sloj ravnomerno je deponovan na kermet sloju bez prisustva neistopljenih čestica.

Troslojni sistem termobarijernih prevlaka ZrO_2 24%MgO/MgZrO₃35%NiCr/ Ni20%Cr deponovan na substratu od legure Al kao termoabrazivne zaštite zadnjih krila aviona J-22 pokazao se kao pouzdana zaštita od temperaturnog mlaza i abrazivnih čestica raketa munje i groma.

Ključne reči: *substrati, zaštita, svojstvo, slojevi, prevlake, barijere, legure.*

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