Microstructure and Mechanical Properties of the Mo-NiCrBSi Coating Deposited by Atmospheric Plasma Spraying

Mihailo Mrdak
Research Associate
IMTEL Microwaves Inc., Belgrade

Aleksandar Vencl
Assistant Professor
University of Belgrade
Faculty of Mechanical Engineering

Milena Ćosić
Lecturer
Tehnikum Taurunum
The College of Mechanical Engineering,
Belgrade

The powder used in this research (Mo-NiCrBSi) was a blend of powders composed of 75 % Mo and 25 % self-fluxing alloy NiCrBSi. With the deposition of this powder a molybdenum base self-fluxing coating is obtained. The process used for coating deposition was atmospheric plasma spraying (APS). The quality of the coatings deposited by APS depends on several parameters such as the sprayed particle size, the deposition temperature, the combustion gases, the feed speed, the angle and rate of deposition (continuous or intermittent), the spray distance, the temperature of the substrate, the pressure applied during the process, etc. All these parameters should be carefully selected in order to obtain the best coating properties for each application. In this research, three groups of the Mo-NiCrBSi coating specimens were produced with different spray distance parameter. Their microstructure and mechanical properties were analysed in order to find the optimal spray parameters i.e the ones that give the best structural and mechanical characteristics of the coating.

Keywords: *atmospheric plasma spraying, molybdenum coatings, microstructure, mechanical properties.*

1. INTRODUCTION

The powder used in this research (Mo-NiCrBSi) was a blend of powders composed of 75 % Mo and 25 % self-fluxing alloy NiCrBSi. With the deposition of this powder a molybdenum base self-fluxing coating is obtained. This coating has high wear resistance, a low coefficient of friction and good scuffing resistance. It can be used for hardfacings, hard bearing surfaces and abrasive wear resistant coatings up to approximately 350 ºC. It is also compatible with the most of the materials, especially with iron-based alloys. These coatings have higher wear resistance (approximately 20 %) and higher tensile bond strength comparing to the pure molybdenum coatings [1].

Amongst the spraying materials, nickel-based alloys are being widely used because they display good resistance to wear, oxidation and high temperature corrosion, as well as being low cost. NiCrBSi alloy is one of the alloys with better performances and it is commonly used in mechanical components such as rollers in cooling tables in hot strip mills, pump bushings and wearing plates [2]. However, improving, for example, the wear resistance of these alloys is still required. Actually, it seems that the tribological performances of such coatings are strongly affected by the presence, the nature, the quantity and the morphology of the second phases [3]. The presence of boron and silicon in its composition lowers the melting point of this type of alloys and gives them the "self-fluxing" character, which is especially suited for plasma spraying or HVOF coating process [4].

Thermal spray is one of the most versatile deposition processes for coating materials and its use for industrial applications has been greatly increased. There are several different processes for thermal spray coating deposition and mostly used are flame spray, electric arc wire spray, plasma spray and high velocity oxy-fuel spray (HVOF) process [5]. The plasma spray process is the most widely used coating method because it presents process flexibility and coating quality in combination [6]. Thermal spraying is, in fact, a generic group of processes in which the coating material is fed to a heating zone, where it becomes molten, and is then propelled to the surface to be coated. Metallic, ceramic, cermets and some polymeric materials can be used in the form of powder, wire, or rod for this purpose [7].

Despite the high temperatures generated by the thermal spray process, some of the powder particles do not melt completely because of the brief time they spend into the plasma flow. Oxidation and limited droplet kinetic energy and temperature lead to non-homogenous coatings with over 3 % porosity and the relatively poor adherence between coating and substrate, which also has a critical impact on tribological performance [8]. Microcracks and porosity are undesired microstructural features because they increase permeability in the application requiring resistance to corrosion [6]. The quality of the coatings manufactured by thermal deposition techniques depends on several parameters such as the sprayed particle size, the deposition temperature, the combustion gases, the feed speed, the angle and rate of deposition (continuous or intermittent), the spray distance, the temperature of the substrate, the pressure applied during the process and, of course, the deposition technique. All these

---

Received: January 2009, Accepted: February 2009
Correspondence to: Dr Mihailo Mrdak
IMTEL Microwaves Inc.,
Bulevar Mihaila Pupina 165b, 11070 Belgrade, Serbia
E-mail: miki@insimtel.com

parameters should be carefully selected in order to obtain the best coating properties for each application [9]. Optimal values of these parameters give optimal structural and mechanical characteristics of the coatings, which is necessary in order to fulfil the required requests.

In this paper, microstructure and mechanical properties of the Mo-NiCrBSi coating deposited by atmospheric plasma spraying (APS) were analysed. Three groups of specimens were produced with different spray distance parameter in order to find the optimal spray parameters i.e. the ones that give the best structural and mechanical characteristics of the coating.

2. THEORETICAL CONSIDERATIONS

The Mo-NiCrBSi coatings arise as a result of a perennial investigation with the aim of the pure Mo coatings tribological properties upgrade. As early as in the year 1973 results of the tests on plasma sprayed coatings of molybdenum powders were published and even at that time a test was made to adjust the coating properties strictly by variation of the powder properties [10].

The NiCrBSi powder, which consists of borides, silicides and carbides phases fine particles is added to the Mo powder in order to increase its hardness and wear resistance. Chemical elements B and C have the strongest influence on the coating hardness since they create borides, carbides and carbo-borides in coating layers. In the NiCr alloy almost the whole content of B is in the state of nickel- and chrome-borides. The Ni-Cr-B ternary alloy phase diagram analysis shows that the alloy must have three phases which consist of nickel-base solid solution Ni(Cr), nickel-boride Ni_3B and chrome-borides CrB and Cr_5B_5. Since the NiCrBSi alloy includes Si and C, a nickel-silicide Ni_5Si_2 and chrome-carbide Cr_7Si_3 are present in the coating layers.

NiCrBSi alloys are the result of adding alloys to traditional Ni-based alloys in order to improve certain properties. Chromium promotes resistance to oxidation and high temperature corrosion and increases the hardness of the coating by forming very hard precipitates. The addition of boron and silicon increases the self-fluxing capabilities of the NiCr alloy, improving its ability to produce coatings by melting process. Carbon produces carbides with high hardness levels that improve the wear resistance of coatings [2]. By adding of the B and Si the melting temperature of NiCr alloy is decreased from 1399 ºC to 1025 ºC. This results in relatively poor alloying of the Mo, which possesses high melting temperature of 2610 ˚C, with the NiCrBSi. Finally, this is the reason why the structure of the Mo-NiCrBSi coating is laminar, consisting of Mo and NiCrBSi layers. The microhardness of the NiCrBSi layers in the coating increases with addition of boron and silicon (Fig. 1). The lower ductility of hard NiCrBSi layers is compensated with the tough Mo layers, which make matrix of the coating.

The Mo-NiCrBSi coatings are homogenous with less than 3 % of porosity and with good adherence between coating and substrate. They do not need additional heat treatment (melting and fusing). The characteristics of the coatings that influence the quality of the coating are distribution of the NiCrBSi layers in Mo matrix, distribution of the Cr, B and Si phases in NiCr layers and distribution of the MoO_3 oxide in Mo layers. Porosity, volume share of the unmelted particles and adhesive/cohesive strength also influence the quality of the obtained coating.

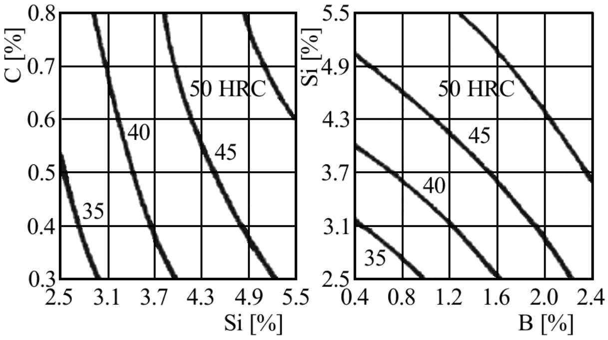

Figure 1. Influence of the alloying elements on the NiCrBSi layers hardness

3. EXPERIMENTAL DETAILS

3.1 Materials

Substrate material was stainless steel containing 13 % chrome (EN 1.4024). The material was used without any heat treatment.

Spray powder used in this experiment was “Metco 505”, which is a commercial brand name of Metco Inc. The powder is a blend of molybdenum and nickel self-fluxing alloy (Mo-NiCrBSi). The share of the individual powder in a blend was 75 % of Mo and 25 % of NiCrBSi. Complete chemical composition of the powder blend is shown in Table 1.

Table 1. Chemical composition of used powder

Element	Mo	Ni	Cr	B	Si	Fe	C
Wt. [%]	75	17.75	4.25	0.8	1.0	1.0	0.2

This spray powder blend was observed with scanning electron microscope (SEM) and it shows spherical morphology with particle granulation –90/+15 μm. Molybdenum powder was produced by agglomeration of the ultra fine particles and associated with special organic binder [11]. Subsequent sintering was provided to form optimal dimension and shape of the powder particles i.e. to get coarser particles (Fig. 2a). NiCrBSi powder was processed by gas atomization of the particles (Fig. 2b).

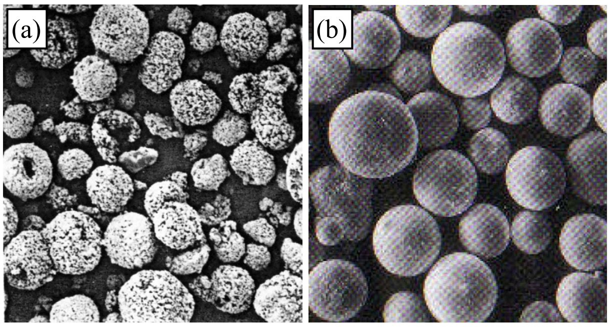

Figure 2. OM micrograph of used powders: (a) Mo powder and (b) NiCrBSi powder

In the APS process the adhesion of the coating to the substrate predominantly consists of mechanical bonding and the pre-treatment of the surface is very important. The surface of the substrate is usually roughened and activated so the area for bonding of the sprayed particles is increased. In this case, before the spraying process, surface of the substrate was activated with white fused alumina (Al_2O_3) using particle sizes of 700 – 1500 μm.

3.2 Spray conditions

Atmospheric plasma spraying (APS), with Sulzer Metco's F4-MB Plasma Spray Gun, was utilized in the experiment. Argon (primary gas) combined with hydrogen (secondary gas) was used as a fuel gas. During the atmospheric plasma spraying process, melted or molten powder material is propelled, by the carrier gas (argon), onto a cleaned and prepared specimen surface. Since the APS coating characteristic (porosity, structure, presence of unmelted particles and oxide inclusions, microhardness, bond strength etc.) are very dependent on spray parameters, they should be carefully chosen. According to some researchers [12], there are more than 50 macroscopic parameters that influence the quality of the coating and the production of coating is still based on trial and error approach.

The high melting temperatures of both blend powders, Mo and NiCrBSi self-fluxing alloy, were considered when the spray parameters were chosen. In order to get the adequate melting of the powders, electric current of 500 A and 64 V was used. Knowing the fact that the percentage of unmelted powder particles in the obtained coating as well as a porosity of the coating strongly depends on the time period the powder particles spent in the plasma flame, spray distance parameter was chosen as a variable in the coating characteristics optimisation process. All the other spray parameters were kept constant during the optimisation process. Altogether, three groups of specimens were produced with the following spray distances: 90 mm, 110 mm and 130 mm.

The target coating thickness for all specimens was 350 – 400 μm. The detailed spray parameters are summarised in Table 2.

Table 2. APS spray parameters used for coating deposition

Parameter	Value
Primary plasma gas (Ar) [l/min]	47
Secondary plasma gas (H_2) [l/min]	10
Electric current [A]	500
Powder carrier gas (Ar) [l/min]	5
Powder feed rate [g/min]	40
Spray distance [mm]	90 / 110 / 130

3.3 Microstructure analysis and tensile bond strength and hardness tests

Microstructural and mechanical characterization of the obtained coatings included metallographic examinations and tensile bond strength and hardness measurements. Characterization was done according to the Pratt & Whitney standard [13]. For the metallographic examination and hardness measurement rectangle specimens 70 mm × 20 mm and 1.5 mm thick were used, while for the tensile bond strength measurement cylindrical specimens Ø25 × 50 mm were used.

The microstructure of the coatings and presence of the cracks were analyzed with optical microscope (OM), where the coatings were sectioned perpendicular to the coated surface. Metallographic samples were prepared in a standard way applying grinding and polishing, with no etching. Percentage share of the pores and unmelted particles in the coatings were measured by image analysis of OM micrographs.

Tensile bond strength tests were performed at room temperature on a hydraulic tensile test rig using a crosshead speed of 10 mm/min for all the tests. The bond strength was calculated by dividing the failure load by the cross-sectional area of the specimen. The geometry of the specimens was according to ASTM C633 standard [14]. Two specimens in pair were used, and the coating was deposited only on one of them. Specimens were bonded by glue and kept pressed against each other in a furnace at a temperature of 180 °C for 2 hours.

Microhardness measurements were carried out using a 1368 Vickers diamond pyramid indenter and 300 g load. Since the coating poses a heterogeneous structure with Mo and NiCrBSi layers, the measurements of both layers were made in order to get hardness distributions per coating layer. The presented results of the testing of tensile bond strength as well as hardness of the coatings represent an average value of a larger number of tests.

4. RESULTS AND DISCUSSION

4.1 Microstructure

Mechanical characteristics of the obtained coatings are in direct correlation with their microstructures. Optical micrographs in Figure 3 show the microstructure of the obtained coatings with three different spray distance parameter used.

In the first coating with 90 mm spray distance (Fig. 3a) high percent share of the unmelted particles could be noticed. Pores are situated between the unmelted particles and they are very coarse and also with high percent share in the coating. Because of the relatively short spray distance and consequently the short time period the powder particles spent in the plasma flame, the powder did not melt completely resulting in a high amount of unmelted particles. This also influenced the coating structure. Elongated splats of molten powder forming a lamellar structure, with oxide layers in between, is a typical structure of thermal spray coatings [15,16]. This type of structure was not noticed with this coating.

With the increase of the spray distance to 110 mm (Fig. 3b) percent share of the unmelted particles as well as amount and size of the pores decrease. Comparing with the coating showed in Figure 3a the spray distance was just 20 mm longer and the unmelted particle amount in the coatings was 70 % lesser. Lower porosity of this coating enables better flow of the molten particles and forming of the typical lamellar structure of Mo and

NiCrBSi layers. Thin dark coloured layers of the MoO_3 oxides inside the Mo layers could also be noticed.

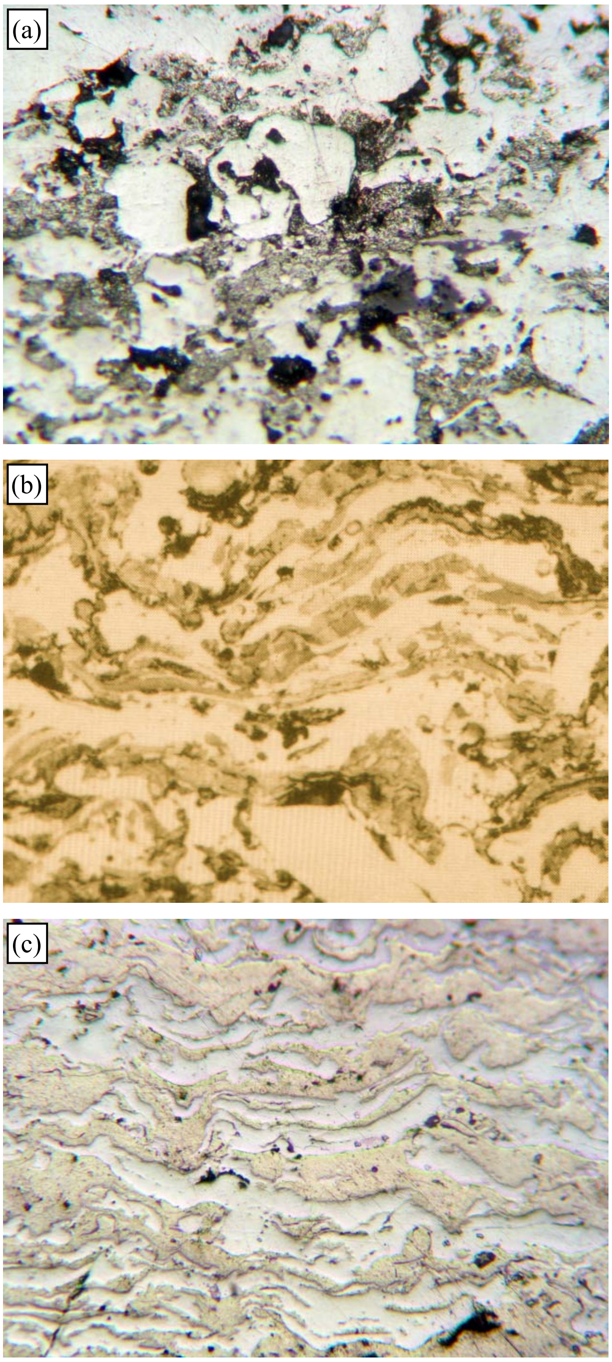

Figure 3. OM cross-section micrograph of the coatings obtained with: (a) 90 mm, (b) 110 mm and (c) 130 mm spray distance; Magnification 400X

In the third coating that was deposited with the highest spray distance of 130 mm (Fig. 3c) also showed typical lamellar structure. Two distinct layer types could be clearly noticed. First type, Mo layers, forms a base of the coating. Inside these layers there are fine and thin MoO_3 oxide layers and micro pores with the percent share of 3 %. Presence of the unmelted particles inside the Mo layers could not be noticed. Second type, NiCrBSi layers, is evenly distributed between the Mo layers. Solid solution of chrome in nickel with presented dispersed phases of the borides, silicides and carbon-borides forms a base of the NiCrBSi layers. Presence of the unmelted particles and micro pores could not be detected in these layers, which indicates adequate melting and flow of the powder.

4.2 Tensile bond strength

The obtained values of tensile bond strength of the coatings with three different spray distance parameters used are shown in Figure 4. The values of all three coatings are in direct correlation with unmelted particles and pores amount in the coatings.

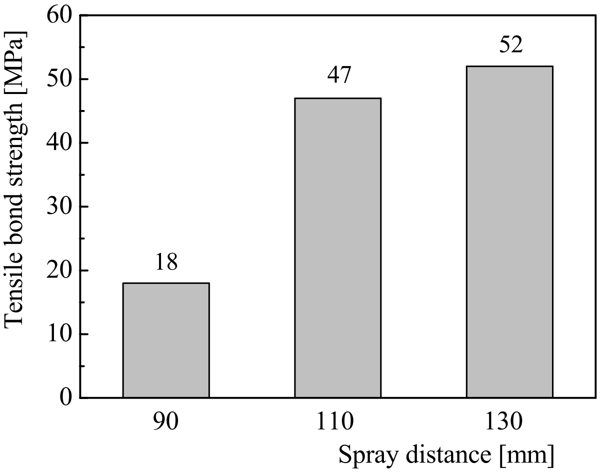

Figure 4. Tensile bond strength of the obtained Mo-NiCrBSi coatings

First coating, with 90 mm spray distance, showed the lowest values of the tensile bond strength (18 MPa) that is lower than the minimum prescribed value for this type of coating (22 MPa) [1]. Also, during the testing, the fracture occurred through the coating, which indicates weak cohesion strength between the layers. These results are in correlation with the microstructure analysis since the presence of unmelted particles and pores were the highest in this coating comparing to the other two coatings.

For the other two coatings the obtained values were in acceptable range for this type of coatings. The third coating that was deposited with the highest spray distance showed the highest values of the tensile bond strength (52 MPa), and, during the testing, the fracture occurred through the coating layers near the coating/substrate interface.

4.3 Microhardness

The obtained values of microhardness of the coatings, depending on the used spray distance are shown in Figure 5. The lower values in the figure refer to the Mo layer microhardness and the higher values refer to the NiCrBSi layers.

Microhardness of the first coating was very low (214 / 323 HV 0.3), and lower than the expected limits for this type of coating. With the increase of the spray distance, the values of the microhardness also increase and the third coating showed the highest values (430 / 729 HV 0.3). Obtained microhardness values are in direct correlation with the coatings microstructure. Relatively high values of the microhardness, which is typical for this type of coatings, could be acquired if the coating poses adequate lamellar structure with high cohesion strength between the layers and high adhesion strength on the coating/substrate interface. The spray distance in the third coating was high enough to enable adequate melting and flow of the powder, and consequently high microhardness values.

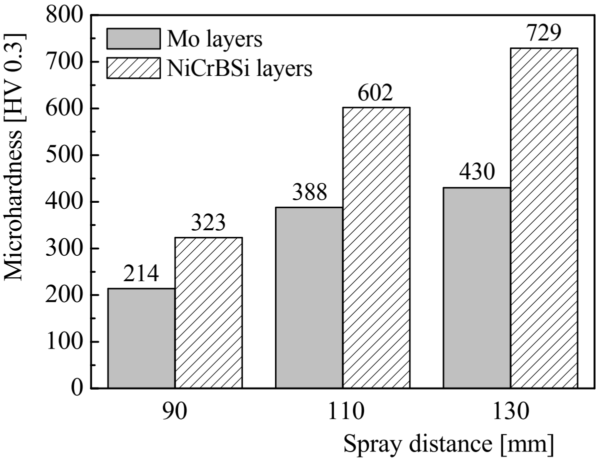

Figure 5. Microhardness of the Mo and NiCrBSi layers in the obtained coatings

5. CONCLUSION

Three Molybdenum based coatings (Mo-NiCrBSi) were deposited by atmospheric plasma spraying with three different spray distances (90, 110 and 130 mm) and their microstructures and mechanical properties were investigated and analysed, with the following conclusions.

Microstructure of the first coating (90 mm) was not satisfactory, while second (110mm) and third (130 mm) coating had a lamellar microstructure, which was typical for this type of coatings. Compared to the second coating, the third coating had better microstructure (smaller content of pores and unmelted particles and better distributions of layers).

Tensile bond strength of the first coating was very low, while for the other two coatings the obtained values were in acceptable range for this type of coatings. The third coating showed the highest values of the tensile bond strength and the fracture occurred through the coating layers near the coating/substrate interface, which is preferable.

The values of the microhardness increased with the increase of the spray distance, and the third coating showed the highest values of microhardness. Both microhardness and tensile bond strength values were in correlation with the coatings microstructure analysis of this i.e. in inverse proportion to the presence of unmelted particles and pores in these coatings.

The third coating, with the 130 mm spray distance, showed the best quality. The characteristics of this coating were better than required for this type of coating, so it was not necessary to take any further tests with a higher spray distance.

REFERENCES

[1] *METCO 505 Self-Fusing High-Molybdenum Blend Powder*, Technical Bulletin, Metco Inc., New York, 1974.

[2] González, R., Cadenas, M., Fernández, R., Cortizo, J.L. and Rodríguez, E.: Wear behaviour of flame sprayed NiCrBSi coating remelted by flame or by laser, Wear, Vol. 262, No. 3-4, pp. 301-307, 2007.

[3] Planche, M.P., Liao, H., Normand, B. and Coddet, C.: Relationships between NiCrBSi particle characteristics and corresponding coating properties using different thermal spraying processes, Surface and Coatings Technology, Vol. 200, No. 7, pp. 2465-2473, 2005.

[4] Tobar, M.J., Álvarez, C., Amado, J.M., Rodríguez, G. and Yáñez, A: Morphology and characterization of laser clad composite NiCrBSi-WC coatings on stainless steel, Surface and Coatings Technology, Vol. 200, No. 22-23, pp. 6313-6317, 2006.

[5] Vencl, A., Mrdak, M. and Cvijović I., 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, 2006.

[6] Samur, R. and Çetiner, B.G.: Quantitative determination of microcracks on ceramic coatings by computer image analysis, Metalurgija, Vol. 44, No. 1, pp. 41-44, 2005.

[7] González, R., García, M.A., Peñuelas, I., Cadenas, M., del Rocío Fernández, Ma., Hernández Battez, A. and Felgueroso, D.: Microstructural study of NiCrBSi coatings obtained by different processes, Wear, Vol. 263, No. 1-6, pp. 619-624, 2007.

[8] Felgueroso, D., Vijande, R., Cuetos, J.M., Tucho, R. and Hernández, A.: Parallel laser melted tracks: Effects on the wear behaviour of plasma-sprayed Ni-based coatings, Wear, Vol. 264, No. 3-4, pp. 257-263, 2008.

[9] Gómez-del Río, T., Garrido, M.A., Fernández, J.E., Cadenas, M. and Rodrígueza, J.: Influence of the deposition techniques on the mechanical properties and microstructure of NiCrBSi coatings, Journal of Materials Processing Technology, Vol. 204, No. 1-3, pp. 304-312, 2008.

[10] Beczkowiak, J.: Hard molybdenum coatings by plasma spraying of unalloyed and oxygen-containing molybdenum powders, in: *Proceedings of the 1st Plasma-Technik-Symposium, Vol. 2*, 18-20.05.1988, Lucerne, Switzerland, pp. 203-211.

[11] Mrdak, M., Kakaš, D. and Popović, Đ.: Characterisation of APS – Mo wear resistant coatings, in: *Proceedings of the 5th International Conference on Tribology – BALKANTRIB ‘05*, 15-18.06.2005, Kragujevac, Serbia, pp. 235-239.

[12] Lugscheider, E., Barimani, C., Eckert, P. and Eritt, U.: Modeling of the APS plasma spray process, Computational Materials Science, Vol. 7, No. 1-2, pp. 109-114, 1996.

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

[14] ASTM C633-01 Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings, Annual Book of ASTM Standards, Vol. 02.05, 2001.

[15] Schorr, B.S., Stein, K.J. and Marder, A.R.: Characterization of thermal spray coatings, Materials Characterization, Vol. 42, No. 2-3, pp. 93-100, 1999.

[16] Hwang, B., Ahn, J. and Lee, S.: Correlation of microstructure and wear resistance of ferrous coatings fabricated by atmospheric plasma spraying, Metallurgical and Materials Transactions A, Vol. 33A, No. 9, pp. 2933-2945, 2002.

МИКРОСТРУКТУРА И МЕХАНИЧКЕ КАРАКТЕРИСТИКЕ Mo-NiCrBSi ПРЕВЛАКЕ НАНЕТЕ ПЛАЗМА СПРЕЈ ПОСТУПКОМ У АТМОСФЕРСКИМ УСЛОВИМА

Михаило Мрдак, Александар Венцл, Милена Ћосић

Прах који је коришћен у овом истраживању (Mo-NiCrBSi) је мешавина два праха, праха Mo и праха „самотекуће“ легуре NiCrBSi, у процентуалном односу 75/25 %. Наношењем ове мешавине прахова добијена је „самотекућа“ превлака на бази молибдена. Превлака је нанета плазма спреј поступком у атмосферским условима. Квалитет овако добијене превлаке зависи од неколико параметара као што су: величина честица праха који се наноси, температура наношења, врста гасова који се користе, количина унетог праха, угао и темпо наношења (континуално или са прекидима), растојање плазма спреј пиштоља од основе, температура основе, примењени притисак током поступка итд. Све ове параметре треба пажљиво изабрати како би се добиле превлаке са најбољим карактеристикама, а у зависности од жељене примене. У овом истраживању су коришћене три групе Mo-NiCrBSi превлака добијене са три различита растојања плазма спреј пиштоља од основе. Микроструктуре и механичке карактеристике добијених превлака су анализиране да би се дошло до оптималних параметара наношења тј. до оних који дају најбоље резултате.