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EFFECT OF HELIUM PLASMA GAS FLOW RATE ON THE PROPERTIES OF WC-12 wt.%Co COATINGS SPRAYED BY ATMOSPHERIC PLASMA

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Summary:

The cermet coatings of WC-12wt.%Co are extensively used to improve the wear resistance of a wide range of technical components. This paper analyses the influence of the plasma gas flow of helium on the microstructure and mechanical properties of WC-12wt.%Co coatings deposited by plasma spraying at atmospheric pressure (APS). In order to obtain homogeneous and denser coatings, three different flows of He (8 l/min., 16 l/min. and 32 l/min.) were used in the research. With the application of He, coatings achieved higher values of hardness due to less degradation of the primary WC carbides. The main goal was to deposit dense and homogeneous layers of WC-12wt.%Co coatings with improved wear resistance for different applications. The test results of the microstructure of the layers were evaluated under a light microscope. The analysis of the microstructure and the mechanical properties of the deposited layers was made in accordance with the standard of Pratt-Whitney. The morphology of the powder particles and the microstructure of the best coating was examined on the SEM (scanning electron microscope). The evaluation of the mechanical properties of the layers was done by applying the $HV_{0.3}$ *method for microhardness testing and by applying tensile testing to test the bond strength. The research has shown that the flow of He plasma gas significantly affects the microstructure, the mechanical properties and the structure of WC-12 wt.%Co coatings.*

Key word: *plasmas, microstructures, mechanical properties, layers, gas flow, flow rate, coatings, Co.*

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Introduction

WC-Co cermet coatings are groups of coatings designed for wide-spectrum abrasion resistance. Thermal spray processes such as plasma spraying APS, VPS and HVOF processes are commonly used for their deposition. These technological processes have proven to be good for the production of WC-Co cermet coatings as a replacement for electrolytic hard chromium, especially in the aerospace industry (Berger, et al., 1996, pp.89-96), (Dorfman, et al., 2000, pp.471-478), (Sartwell, et al., 2002), (Savarimuthu, et al., 2000, pp.1095-1104). Thermally sprayed WC-Co coatings are used extensively to improve the abrasion resistance of technical components. WC-Co coatings deposited with thermal spraying are widely used in the cases when high resistance to abrasion and erosion resistance are requested. These coatings exhibit higher phase microstructures which are formed from the WC primary carbides such as W_2C, W and amorphous phases of Co-based binders (Li, et al., 1996, p.785), (Verdon, et al., 1998, p.11). The microstructure of WC-Co coatings has three crystalline phases (WC, W_2C and W). The WC carbide phase is present in the initial powder but the other two phases are formed during the spraying process through decarburization of WC carbideparticles. The share of the secondary phases (W_2C and W) was higher in the coatings sprayed using hydrogen H_2 as plasma gas. Hydrogen has a high heat content – enthalpy and therefore there is greater decarburization of WC carbide particles. The porosity of the coatings produced is about 10%. In these coatings, the presence of a matrix rich in Co was identified. This Co-rich phase represents the areas with different composition. The bright fields belong to the matrix areas with a high percentage of W. WC grains are within the splats where the temperature achieved is not high enough to produce the collapse of grains. The W_2C carbide phase was identified around WC grains. The metal W was discovered in the outer part of the splats where decarburization is higher. The reason for this may be a larger share of W_2C and higher strenghtening of the Co matrix with the desintegration of WC carbides. When He is used as plasma gas, coatings achieve higher hardness values due to a higher content of primary non decomposed WC carbide grains. The He gas has a lower enthalpy value than H_2 and makes denser plasma which absorbs less oxygen (Mrdak, 2012, pp.71-89), (Mrdak, 2013, pp.68-88), which results in the smaller decomposition of WC grains; therefore,the coating in the structure retains a higher number of primary WC grains. The increase of the coating microhardness is expected when the proportion of WC grains in the microstructure is higher. The highest values of hardness and toughness of the coating are achieved when He is used as plasma gas. These values are similar to those obtained in the coatings sprayed with the HVOF process (Khameneh Asl, Heydarzadeh Sohi, 2006, pp.1203-1208). With the development of the cold spray, there is a possibility for carbide decarburization to be eliminated, completely or partially, since the spraying of particles takes place at lower temperature (Jodoin, et al., 2006, pp.4424-4432), (Kim, et al., 2005, pp.243-248), (Lima, et al., 2002), (Li, et al., 2007, pp.1011-1020), (Papyrin, 2001, pp.49-51), (Stoltenhoff, et al., 2002, pp.542-550). Using powders with a reduced WC grain size improves the properties such as hardness and toughness, even resistance to sliding (Jia, Fischer, 1996, pp.206-214) and resistance to wear (Jia, Fischer, 1997, pp.310-318). A significant effort has been devoted to studying the effect of the percentage of binder phase and spraying conditions on the properties of coatings (Dent, et al., 2002, pp.551-558), (Qiao, et al., 2003, pp.24-41), (Marple, Lima, 2003, pp.273-282). In these studies, it was found that the adhesion and the level of decarburization affect significantly the microstructure and properties of coatings. Decarburization affects not only hardness, but also wear, as suggested by Qiao et al.; therefore, the optimization of parameters it is very important (Qiao, et al., 2003, pp.24-41). The reaction of the WC carbide decomposition takes place during thermal spraying (Guilemany, et al., 1999, pp.1913-1921), by the reaction:

$$2WC + O_2 \leftrightarrow W_2C + CO_2 \qquad \text{(Eq 1)}$$

$$W_2C + 1/2O_2 \leftrightarrow W_2(CO) \qquad \text{(Eq 2)}$$

$$W_2(CO) \leftrightarrow 2W + CO \qquad \text{(Eq 3)}$$

Chemical reactions take place in WC carbide primary grains that interact with oxygen. Also, WC carbide primary grains can be degraded in the atmosphere without oxygen in accordance with equation 4:

$$2WC \leftrightarrow W_2C + C \qquad \text{(Eq 4)}$$

According to some authors (Guilemany, et al., 1999, pp.1913-1921), (Verdon, et al., 1998, pp.11-24), two types of W_2C carbide can be formed. The first type is formed when the primary grains of WC carbides decompose in accordance with equations Eq 1 or Eq 4. The second mechanism occurs during the solidification of the Co-rich matrix , which leads to the precipitation of the W_2C phase on the WC grain boundaries. Later,W_2C phases appear as globular edges around WC grains. As a result of the decomposition reactions, some carbon is dissolved in the matrix, and some reacts with oxygen from the surface to form CO/CO_2, thus losing a part of carbon from the starting powder. The retained C in the matrix, together with W present in the liquid, Eeriches the Co matrix forming amorphous compounds and nanocrystalline regions (Verdon, et al., 1998, pp.11-24), (He, Schoenung, 2002, pp.274-319). Depending on the decarburization degree, metal W can be deposited near the lamella boundaries (Qiao, et al., 2003, pp.24-41) where the carbon envelope is,due to the reaction with oxygen. Also, depending on the degree of decarburization, the precipitation of the η - phase can also occur in the following way (Guilemany, et al., 1999, pp.1913-1921):

$4Co + 4WC + O_2 \leftrightarrow 2Co_2W_4C + 2\,CO$ (Eq 5)

$3Co + 3WC + O_2 \leftrightarrow Co_3W_3C + 2\,CO$ (Eq 6)

$12Co + 12WC + 5O_2 \leftrightarrow 2Co_6W_6C + 10CO$ (Eq 7)

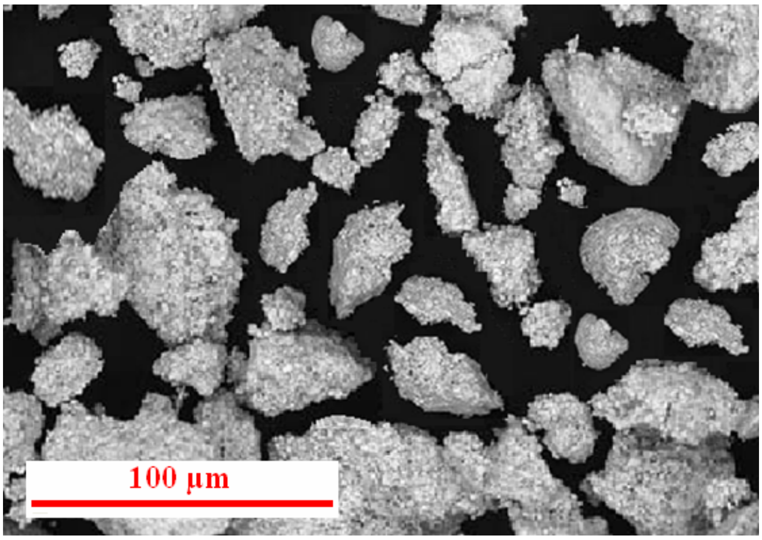
This experimental observation has been confirmed in the coatings with a higher content of decarburization and cracks (Sobolev, et al., 2004).

Sintered and crushed powder of WC– 12wt.%(88WC/12Co) is most often deposited by atmospheric plasma spraying – APS process or by HVOF for the production of very dense WC coatings. These coatings provide excellent resistance to most forms of abrasive wear at temperatures ≤ 500°C (Material Product Data Sheet, 2012, Metco 72F- NS Tungsten Carbide – 12% Cobalt Sintered and Crushed Powders, DSMTS-0115.0, Sulzer Metco). These coatings contain fine WC carbide grains for abrasive resistance against abrasive impact of hard particles, hard surfaces, erosive particles and mechanisms of wear by friction. Coatings are intended for use in dry non-corrosive environments. In comparison with the WC coatingswith 17 wt% of cobalt, the reduced Co content in the coating reduces toughness while increasing hardness and resistance to friction and wear. WC-12wt.%(88WC/12Co) coatings are used on parts such as: conveyor screws, compressor stators, impeller shafts, fan blade midspan supports, exhaust fans, etc. (Material Product Data Sheet, 2012, Metco 72F- NS Tungsten Carbide – 12% Cobalt Sintered and Crushed Powders, DSMTS-0115.0, Sulzer Metco). Mann and al. showed that WC-12wt.%Co coatings significantly increase the erosion resistance of components in the oil industry, such as valves and valve rings (Mann et al., 2006, pp.75-82).

The main objective of this study was to deposit, by atmospheric plasma spraying – APS, dense and homogeneous layers of WC - 12wt.%Co coatings with high resistance to wear and erosion for different applications. When choosing the parameters, He was used as plasma gas; unlike H_2 , He does not react with the powder. It produces denser plasma with a lower heat content which reduces the temperarture of decomposition and decarburization of WC carbide. Three groups of samples were made with a secondary plasma gas flow rate He of 8 l/min., 16 l/min. and 32 l/min. The microstructure and mechanical properties of coating layers were analysed and studied. The best performance was found in layers deposited with a flow rate of He 32 l/min.

Materials and experimental details

WC-12wt.%Co coatings were made with powder Metco 72F – NS (Material Product Data Sheet, 2012, Metco 72F - NS Tungsten Carbide – 12% Cobalt Sintered and Crushed Powders, DSMTS-0115.0, Sulzer Metco). The powder is produced by sintering WC mono carbide particles and metal Co particles and subsequent crushing of sintered particles to obtain specific granulation. The powder used in the experiment had a grain size range of 11 - 45 um. The melting temperature of the powder is 1250°C. Fig. 1 shows a (SEM) scanning electron micrograph of the morphology of powder particles. Irregularly shaped grains of powder WC-12 wt.%Co can be seen.



Slika 1 – (SEM) Skening elektronska mikrografija čestica praha WC – 12 tež.%Co
Figure 1 – (SEM) Scanning electron micrograph of WC – 12 wt.%Co powder particles

The substrates for depositing coatings for testing microhardness and assessing their structure are made of steel Č.4171 (X15Cr13 EN10027) in the thermally unprocessed state, with the dimensions 70x20x1.5mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). The substrates for testing bond stren-gthare also made of steel Č.4171(X15Cr13EN10027) in the thermally unprocessed state, with the dimensions Ø25x50 mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

The mechanical properties of the layers were evaluated by testing hardness using the $HV_{0.3}$ method and by testing their bond strength using tensile testing. Microhardness measurement was performed in the direction along the lamellae, in the middle and at the ends of the samples.Five values were obtained and averaged. Bond strength was tested by tensile testing. The testing was done at room temperature with a tensile speed of 1cm/60s. For each group of samples, three test specimens were tested, and in this paper the mean values are presented.

The microstructural analysis of the coatings was performed under a light microscope. The morphology of the powder particles and the best coating microstructure were done on the SEM (Scanning Electron Microscope).

Layers were applied on the metal substrate using the APS method. The coatings were deposited on steel bases roughed with white electocorundum with a grain size of 0.7 mm to 1.5 mm. For the production of coatings, the atmospheric plasma spray (APS) system of the company Plasmadyne was used. The system consists of: cathode K1083 -129, anode A 2083 -129 and gas injector GI 2083 -130. The main parameter when choosing powder deposition parameters was the plasma gas flow of He (l/min.). Helium was used in a combination with argon gas and an arc power supply of 40 kW. Three groups of samples with three He flows of 8 l/min., 16 l/min. and 32 l/min were made. The layers were deposited on the substrates of a total thickness of 0.15 to 0.18 mm. The detailed values of the plasma spray deposition parameters are shown in Table 1.

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

Deposition parameters	Values		
Plasma current, I (A)	800	800	800
Plasma Voltage, U (V)	32	32	32
Primary plasma gas flow rate, Ar (l/min)	47	47	47
Secondary plasma gas flow rate, He (l/min)	8	16	32
Carrier gas flow rate, Ar (l/min)	7	7	7
Powder feed rate (g/min)	50	50	50
Stand-off distance (mm)	80	80	80

Results and discussion

The measured values of the microhardness of the WC - 12 wt.% Co coating depending on the flow of helium are presented in Fig. 1. The values of the microhardness of the layers of WC- 12 wt.%Co are directly related to the flow of helium. The layers deposited at a flow rate of helium of 8 l/min. had the lowest values of microhardness in the range of 598 - 876$HV_{0.3}$. The highest microhardness values of 997 - 1420$HV_{0.3}$ were observed in the layers with the highest helium flow of 32 l/min. The values of the microhardness of the WC - 12 wt.%Co coatings deposited with a helium flow of 16 l/min. and 32 l/min. were in accordance with the values set by the standard PWA(min. 700$HV_{0.3}$) for this type of coatings (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). The helium flow affected the density of the deposited layers. A small flow of helium resulted in less melting and lower deformation of hard particles during the impact with a previously deposited layer. Limited deformation of particles in the impact with the substrate, which is also less deformed under the impact of depositing particles due to its hardness, causes more porous coating layers. Layers deposited with a high flow of helium are denser as confirmed by the metallographic examination of the samples. Higher values of the microhardness of the WC - 12wt.%Co layers deposited with a higher flow of helium indicate a higher cohesive strength of the layers, as confirmed by the results of tensile bond strength.

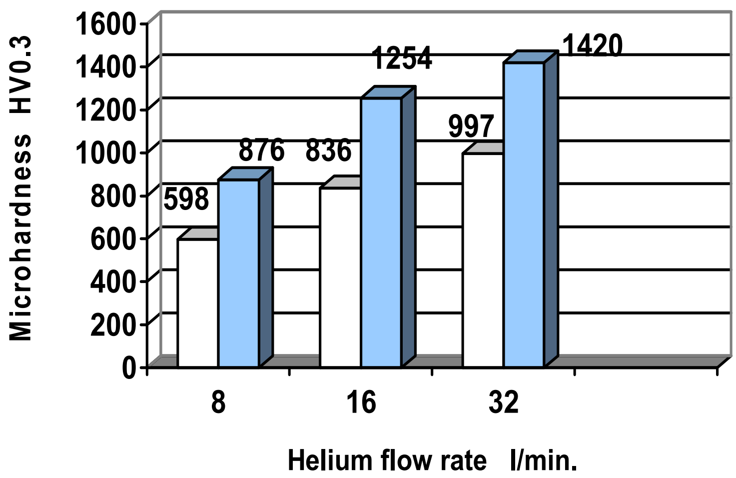


Figure 2 – Microhardness of WC – 12 wt.%Co layers
Slika 2 – Mikrotvrdoća WC – 12tež. %Co slojeva

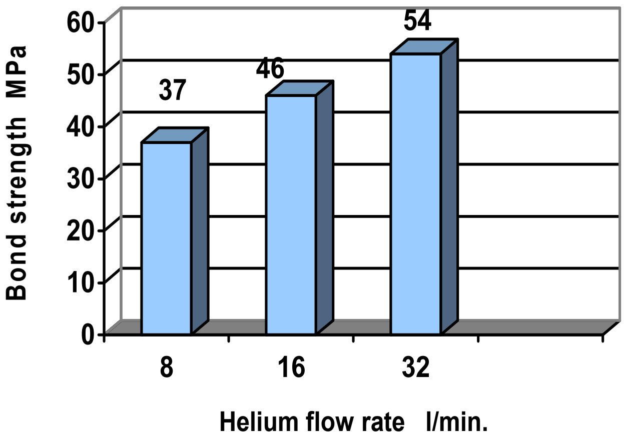


Figure 3 – Bond strength of WC – 12 wt.%Co layers
Slika 3 – Čvrstoća spoja WC – 12tež. %Co slojeva

The tensile bond strength values of WC - 12wt.%Co coatings directly depend on the flow of helium (Fig. 2). As seen in the figure, the helium flow rate affects the values of tensile bond strength. The coatings deposited with the highest helium flow rate of 32 l/min. which had the highest values of microhardness of 997 - 1420$HV_{0.3}$, had the highest tensile bond strength of 54MPa. The layers deposited with the smallest helium flow of 8 l/min. have the smallest minimum tensile bond strength of 37MPa. The tensile bond strength values of the coatings deposited with a helium flow rate of 16 l/min. and 32 l/min. were in accordance with the values set by the standard PWA (45MPa)(Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). During the testing of the samples, a fracture occurred along the coating / substrate interface in all samples. This suggests that the WC – 12wt.%Co coating has a good cohesive strength.

Fig. 4 shows the microstructure of WC -12wt.%Co coatings deposited with the smallest helium flow rate of 8 l/min. The boundaries on the interface between the substrate and the coating layers are very clean, indicating a good substrate surface preparation. The bond of the coating with the substrate is uniform, without separation of coating layers from the substrate. The layers were deposited without the presence of microcracks and macrocracks. In the microstructure of the coatings, black micro pores of irregular shape were most pronounced, due to which the coating has the lowest value of microhardness of 598 - 876$HV_{0.3}$. The coating shows a structure with a limited inter-lamellar bonding, because of volume errors which, in operational conditions, can cause the appearance of micro-cracks and accelerate coating wear.

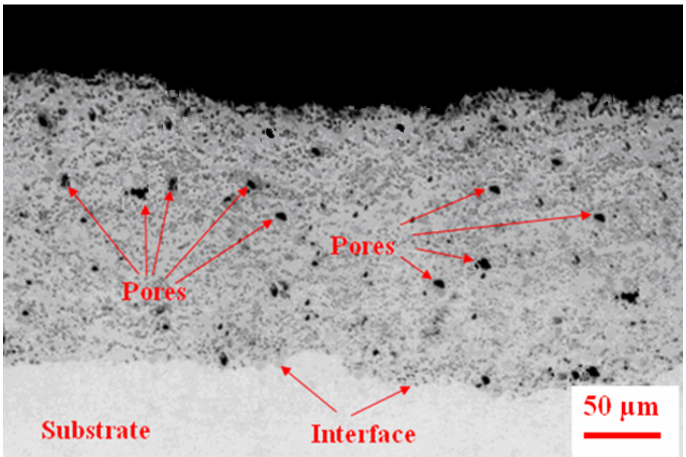


Figure 4 – Microstructure of the WC – 12wt.%Co coating deposited with a helium feed rate of 8 l/min
Slika 4 – Mikrostruktura WC-12tež.%Co prevlake deponovane sa protokom helijuma 8 l/min

Figs. 5 and 6 show the microstructures of the layers of WC-12wt.%Co coatings deposited with a helium flow of 16 l/min. Because of the higher flow of helium, powder particles melt better and deform plastically during theimpact with the substrate, resulting in lower porosity in the coating layers. Fig. 6 clearly shows the black fields of pores. Unmelted powder particles are not present in the microstructure. In the deposited state, powder particles of WC-12wt.%Co are well melted and mutually interconnected to make continual and continuous coating layers (Fig. 6).

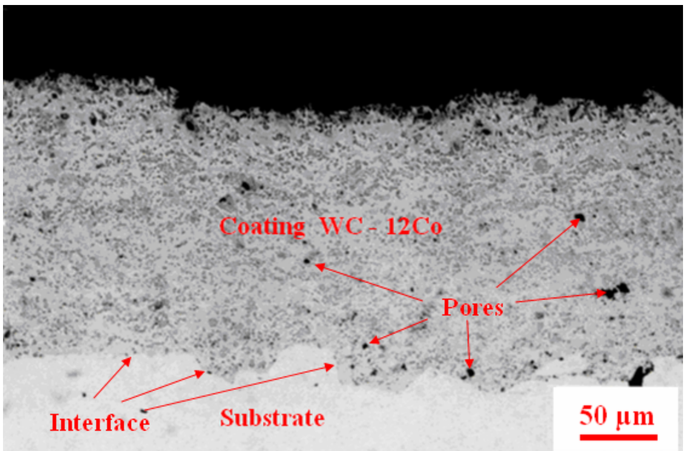


Figure 5 – Microstructure of the WC – 12wt.%Co coating deposited with a helium feed rate of 16 l/min
Slika 5 – Mikrostruktura WC – 12tež.%Co prevlake deponovane sa protokom helijuma 16 l/min

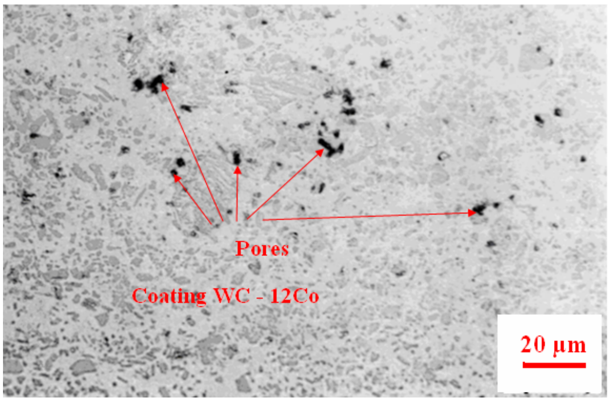


Figure 6 – Microstructure of the WC – 12wt.%Co coatingdeposited with a helium feed rate of 16 l/min
Slika 6 – Mikrostruktura WC – 12tež.%Co prevlake deponovane sa protokom helijuma 16 l/min

Figs. 7 and 8 show the layers of WC-12 wt.%Co coatings deposited with the highest helium flow of 32 l/min. These layers had the best microstructure and mechanical properties. The photomicrograph 7 shows the interface between WC-12wt.% Co layers and the substrate indicating a very good layer-substrate bond, which is consistent with the values of tensile bond strength. Through the coating layers fine micro pores are observed without the presence of coarse pores, which is consistent with the mechanical characteristics of the layers. Unmelted powder particles are not present in the microstructure. In the deposited state, the WC-12wt.% Co powder particles are well melted and interconnected to make continual and continuous coating layers. The WC-12 wt.% Co powder particles are evenly melted and properly deposited in the coating layers.

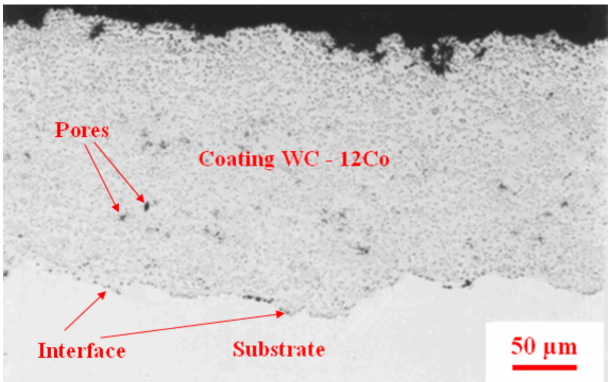


Figure 7 – Microstructure of the WC – 12wt.%Co coating deposited with a helium feed rate of 32 l/min.
Slika 7 – Mikrostruktura WC – 12tež.%Co prevlake deponovane sa protokom helijuma 32 l/min.

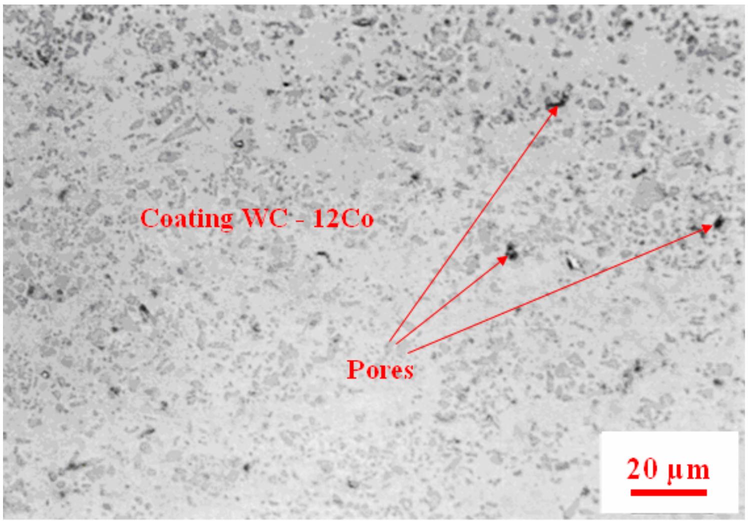


Figure 8 – Microstructure of the WC – 12wt.%Co coating deposited with a helium feed rateof 32 l/min

Slika 8 – Mikrostruktura WC – 12tež.%Co prevlake deponovane sa protokom helijuma 32 l/min

Fig. 8 shows the SEM micrographs of WC-12wt.%Co coatings deposited with a helium flow of 32 l/min. with visible phases present in the microstructure.

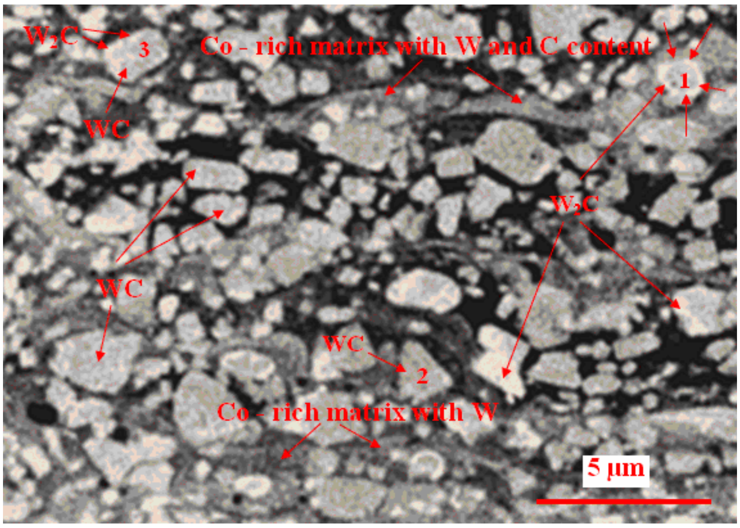


Figure 9 – SEM microstructure of the WC – 12wt.%Co coating deposited with a helium feed rate of 32 l/min

Slika 9 – (SEM) Mikrostruktura WC – 12tež.%Co prevlake deponovane sa protokom helijuma 32 l/min

Due to the decomposition of the primary WC carbide, which cannot be avoided in the process of deposition, the coating shows a multiphase microstructure. In the microstructure, there are angularly shaped grains of the undecomposed primary WC carbide WC (point 2). Decomposition of primary WC carbides results in grains obtaining smoother edges. The formed W_2C carbide concentrates in the form of globules on the edges or the surface of the primary WC carbide grains (point3). Some primary WC carbide grains can be completely surrounded by W_2C carbide (point 3). The primary WC carbide is dark gray, and the W_2C carbide is light white (Li, et al., 1996, p.785), (Verdon, et al., 1998, p.11).Three crystalline phases (WC, W_2C and W dissolved in Co binder base) are present in the microstructure. As a result of the decomposition reaction, some carbon C dissolves in the Co base, and some reacts with oxygen to form CO/CO_2; a share of carbon C from the initial powder is therefore lost. The retained C in the Co base with W enriches the Co base (He, Schoenung, 2002, pp.274-319), (Verdon, et al., 1998, pp.11-24). Depending on the decarburization, metal W can be deposited near the lamella boundary (Qiao, et al., 2003, pp.24-41).

Conclusion

WC-12wt.% Co coatings were deposited by APS - atmospheric plasma spraying with three helium flows of 8 l/min., 16 l/min. and 32 l/min. The microstructure and the mechanical properties of the deposited coatings were analysed and the following conclusions were made.

The mechanical properties and the microstructure of WC-12wt.%Co coatings were directly dependent on the flow rate of helium plasma gas. The increased helium flow led to the deposition of the coatings with higher values of microhardness and tensile bond strength. The coatings deposited with the highest helium flow of 32 l/min. had the highest values of microhardness and tensile bond strength. In all coatings,fractures occurred at the interface between the coating and the substrate. The microhardness and tensile strength values of the bonds were consistent with their microstructures.

Black pores were present in the coating microstructures. The pores were least pronounced in the layers of the coating deposited with a helium flow of 32 l/min. In these layers, fine micro pores are present without the presence of coarse pores, which is consistent with the microstructure and mechanical properties of the layers. The most prominent and the roughest micro pores were in the layers deposited with a helium flow of 8 l/min.

In the microstructure there are the crystalline phases of WC, W_2C and W dissolved together with C in the Co binder base. The dissolved W with C in the Co binder base enriches the Co base. The coatings deposited with a helium flow of 32 l/min. showed the best mechanical properties and microstructure.

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UTICAJ PROTOKA PLAZMA GASA HELIJUMA NA SVOJSTVA WC-12 WT.%CO PREVLAKE NAPRSKANE ATMOSFERSKOM PLAZMOM

OBLAST: hemijske tehnologije
VRSTA ČLANKA: originalni naučni članak

Sažetak:

Kermet prevlake WC-12tež.%Co intenzivno se koriste za poboljšanje otpornosti na habanje širokog spektra tehničkih komponenti. U radu je analiziran uticaj protoka plazma gasa helijuma na mikrostrukturu i me-

hanične karakteristike WC-12tež.%Co prevlaka deponovanih plazma-sprej postupkom na atmosferskom pritisku (APS). Radi dobijanja homogenih i gušćih prevlaka u istraživanju su se koristila tri različita protoka He od 8 l/min., 16 l/min. i 32 l/min. Sa primenom He prevlake postižu veće vrednosti mikrotvrdoće zbog manje razgradnje primarnog karbida WC. Glavni cilj bio je da se deponuju gusti i homogeni slojevi WC-12tež.%Co prevlake sa poboljšanom otpornošću na habanje za različite aplikacije. Rezultati ispitivanja mikrostrukture slojeva procenjeni su na svetlosnom mikroskopu. Mikrostrukturna analiza i mehaničke karakteristike deponovanih slojevima urađene su u skladu sa standardom Pratt-Whitney. Morfologija čestica praha i mikrostruktura najbolje prevlake urađena je na SEM-u (skening elektronskom mikroskopu). Procena mehaničkih karakteristika slojeva urađena je ispitivanjem mikrotvrdoće metodom $HV_{0.3}$ i čvrstoće spoja ispitivanjem na zatezanje. Istraživanje je pokazalo da protok plazma gasa He bitno utiču na mikrostrukturu i mehaničke osobine i strukture WC-12tež.%Co prevlake.

Uvod

Kermet prevlake WC-Co jesu grupe prevlaka namenjene za otpornost na habanje širokog spektra. Za deponovanje se najčešće koriste termički postupci prskanja, kao što su plazma prskanje APS, VPS i postupak HVOF. Ovi tehnološki procesi pokazali su se dobrim za izradu kermet prevlaka WC-Co kao zamena elektrolitičkom tvrdom hromu, posebno u vazduhoplovnoj industriji (Berger, et al., 1996, pp.89-96), (Dorfman, et al., 2000, pp.471-478), (Sartwell, et al., 2002), (Savarimuthu, et al., 2000, pp.1095-1104). U mikrostrukturi preprevlaka WC-Co su prisutne tri kristalne faze (WC, W_2C i W). Karbidna faza WC prisutna je u početnom prahu, ali druge dve faze se formiraju tokom procesa prskanja kroz dekarburizaciju čestica karbida WC. Udeo sekundarnih faza (W_2C i W) veći je u prevlakama naprskanim korišćenjem vodonika H_2 kao plazma gasa. Vodonik ima visok sadržaj toplote – entalpiju, pa zbog toga dolazi do veće dekarburizacije čestica karbida WC. Kada se He koristi kao plazma gas, prevlake postižu veće vrednosti mikrotvrdoće zbog većeg sadržaja primarnih nerazgrađenih karbidnih zrna WC. Gas He ima manju entalpiju od H_2 i pravi gušću plazmu koja manje usisava kiseonik (Mrdak, 2012, pp.71-89), (Mrdak, 2013, pp.68-88), što utiče na manje raspadanje zrna WC, pa prevlaka u strukturi zadržava veći broj primarnih WC zrna. Dekarburizacija ne utiče samo na tvrdoću, već i na habanja, kao što navodi Qiao et al., i zbog toga je optimizacija parametara od velikog značaja (Qiao, et al., 2003, pp.24-41). Reakcija razgradnje karbida WC odvija se tokom termičkog prskanja (Guilemany, et al., 1999, pp.1913-1921), po reakciji:

$$2WC + O_2 \leftrightarrow W_2C + CO_2 \quad \text{(Jn 1)}$$

$$W_2C + 1/2O_2 \leftrightarrow W_2(CO) \quad \text{(Jn 2)}$$

$$W_2(CO) \leftrightarrow 2W + CO \quad \text{(Jn 3)}$$

Hemijske reakcije odvijaju se u zrnima primarnog karbida WC koji je u interakciji sa kiseonikom. Takođe, zrna primarnog karbida WC mogu biti degradirana u atmosferi bez kiseonika po jednačini 4:

$$2WC \leftrightarrow W_2C + C \qquad (Jn\ 4)$$

Prema autorima (Guilemany, et al., 1999, pp.1913-1921), (Verdon, et al., 1998, pp.11-24) mogu se formirati dve vrste karbida W_2C. Prvi tip se formira kada se primarna zrna WC karbida razlažu po jednačinama 1 ili 4. Drugi mehanizam se odvija tokom očvršćavanja matrice bogate Co, što dovodi do taloženja W_2C faze na granicama WC zrna. Kasnije se W_2C faze pojavljuju kao globularne ivice oko WC zrna. Kao posledica ovih reakcija razlaganja nešto ugljenika se rastvara u matrici, a nešto reaguje sa kiseonikom iz površine formirajući CO/CO_2, čime se gubi deo ugljenika iz polaznog praha. Zadržani C u matrici sa W, prisutnim u tečnosti, obogaćuje matricu Co, stvarajući amorfna jedinjenja i nanokristalne regione (Verdon, et al., 1998, pp.11-24), (He, Schoenung, 2002, pp.274-319).

Takođe, u zavisnosti od stepena dekarburizacije, može se odvijati i taloženje η-faza na sledeći način Guilemany, et al., 1999, pp.1913-1921):

$$4Co + 4WC + O_2 \leftrightarrow 2Co_2W_4C + 2\ CO \qquad (Jn\ 5)$$

$$3Co + 3WC + O_2 \leftrightarrow Co_3W_3C + 2\ CO \qquad (Jn\ 6)$$

$$12Co + 12WC + 5O_2 \leftrightarrow 2Co_6W_6C + 10CO \qquad (Jn\ 7)$$

Ovo eksperimentalno zapažanje potvrdilo se u prevlakama sa povećanom dekarburizacijom i većim sadržajem prskotina (Sobolev, et al., 2004).

Prah WC-12tež.% (88WC/12Co) sinterovani i mleveni se najčešće deponuje atmosferski plazma-sprej postupkom – APS ili HVOF za proizvodnju veoma gustih volframkarbid prevlaka. Ove prevlake pružaju odličnu otpornost na većinu oblika abrazionog habanja na temperaturama ≤ 500°C (Material Product Data Sheet, 2012, Metco 72F- NS Tungsten Carbide – 12% Cobalt Sintered and Crushed Powders, DSMTS-0115.0, Sulzer Metco).

Glavni cilj rada bio je da se atmosferskim plazma-sprej postupkom – APS deponuju gusti i homogeni slojevi WC – 12tež.%Co prevlake sa visokom otpornošću na habanje i eroziju za različite aplikacije. Pri izboru parametara kao plazma gasa se koristio He, koji za razliku od H_2 ne reaguje sa prahom, proizvodi gušću plazmu sa manjim toplotnim sadržajem što smanjuje temperarturno razlaganje i dekarburizaciju karbida WC. Urađene su tri grupe uzoraka sa protokom sekundarnog plazma gasa He od 8 l/min, 16 l/min i 32 l/min. Analizirane su i proučavane mikrostrukture i mehaničke karakteristika slojeva prevlaka. Najbolje perfomanse su pokazali slojevi deponovani sa protokom He od 32 l/min.

Materijali i eksperimentalni detalji

Za izradu WC-12tež.%Co prevlaka upotrebljen je prah Metco 72F – NS (Material Product Data Sheet, 2012, Metco 72F – NS Tungsten Carbide – 12% Cobalt Sintered and Crushed Powders, DSMTS-0115.0, Sulzer Metco). Prah je proizveden tehnikom sinterovanja čestica monokarbida WC i metalnih čestica Co i naknadnim mlevenjem sinterovanih čestica na određenu granulaciju. Prah koji se koristio u eksperimentu imao je raspon granulacije od 11 do 45 µm.

Osnove na koje su deponovane prevlake za ispitivanje mikrotvrdoće i za procenu strukture su napravljeni 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). Za ispitivanje čvrstoće spoja su osnove takođe napravljene od čelika Č.4171(X15Cr13EN10027) u termički neobrađenom stanju dimenzija Ø25x50 mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

Procena mehaničkih osobina slojeva urađena je ispitivanjem mikrotvrdoće metodom $HV_{0.3}$ i čvrstoće spoja ispitivanjem na zatezanje. Merenje mikrotvrdoće izvršeno je u pravcu duž lamela, u sredini i na krajevima uzoraka. Urađeno je pet očitavanja vrednosti koje su usrednjene. Metoda ispitivanja čvrstoće spoja je metoda ispitivanja na zatezanje. Ispitivanje je urađeno na sobnoj temperaturi sa brzinom zatezanja 1 cm/60 s. Za svaku grupu uzoraka ispitane su po tri epruvete, a u radu su prikazane srednje vrednosti.

Mikrostrukturna analiza prevlaka urađena je na svetlosnom mikroskopu. Morfologija čestica praha i mikrostruktura najbolje prevlake urađena je na SEM-u (skening elektronskom mikroskopu).

Proces nanošenja slojeva na metalne osnove urađen je plazma-sprej postupkom na atmosferskom pritisku (APS). Prevlake su deponovane na čelične osnove koje su ohrapavljene belim elektrokorundom granulacije od 0,7mm do 1,5 mm. Za proizvodnju prevlaka koristio se atmosferski plazma-sprej sistem (APS) firme Plasmadyne, koji se sastojao od: katode tip K1083 -129, anode tip A 2083 -129 i gas injektora tip GI 2083 -130. Pri izboru parametara depozicije praha kao osnovni parameter uzet je protok plazma gasa He (l/min). Helijum je korišćen u kombinaciji sa lučnim gasom argon uz snagu napajanja od 40 KW. Urađene su tri grupe uzoraka sa tri protoka He od 8 l/min, 16 l/min i 32 l/min. Slojevi su deponovani na supstratima ukupne debljine od 0,15 do 0,18 mm.

Rezultati i diskusija

Slojevi deponovani sa protokom helijuma od 8 l/min imali su najniže vrednosti makrotvrdoće u rasponu od 598 do 876HV $_{0.3}$. Najviše vrednosti mikrotvrdoće od 997 do 1420$HV_{0.3}$ izmerene su u slojevima sa najvećim protokom helijuma od 32 l/min. Vrednodti mikrotvrdoće WC – 12tež.%Co prevlaka deponovanih sa protokom helijuma od 16 l/min i 32 l/min bile su u skladu sa vrednostima koje propisuje standard

PWA(min. 700HV0.3) za ovaj tip prevlake (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). Protok helijuma uticao je na gustinu deponovanih slojeva. Mali protok helijuma uticao je na slabije topljenje i slabiju deformaciju tvrdih čestica u sudaru sa prethodno deponovanim slojem. Prevlake deponovane sa najvećim protokom helijuma od 32 l/min koji su imali najveće vrednosti mikrotvrdoće od 997 do 1420$HV_{0.3}$ imali su najveću zateznu čvrstoću spoja od 54MPa. Slojevi deponovani sa najmanjim protokom helijuma od 8 l/min imaju najmanju zateznu čvrstoću spoja od 37MPa. Vrednosti zatezne čvrstoće spoja prevlaka deponovanih sa protokom helijuma od 16 l/min i 32 l/min bile su u skladu sa vrednostima koje propisuje standard PWA (45MPa)(Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). Tokom testiranja uzoraka za sve uzorke prelom se dešavao duž interfejsa prevlaka/supstrat. To ukazuje da je dobra koheziona čvrstoća WC – 12tež.%Co prevlaka.

Granice na interfejsu između substrata i slojeva prevlake izuzetno su čiste, što ukazuje na dobru pripremu površine substrata. Veza prevlake sa substratom je uniformna bez odvajanja slojeva prevlake sa substrata. Slojevi su deponovani bez prisustva mikropukotina i makropukotina. U mikrostrukturi prevlake deponovane sa protokom helijuma od 8 l/min ima najizražajnije mikropore crne boje nepravilnog oblika, koje su uticale na to da prevlaka ima najniže vrednosti mikrotvrdoće od 598 do 876$HV_{0.3}$. Prevlaka pokazuje strukturu sa ograničenom interlamelarnim vezivanjem, zbog zapreminskih grešaka koje u radnim uslovima mogu uzrokovati pojavu mikropukotina i ubrzati habanje prevlake. Slojevi WC-12 tež.%Co prevlake deponovane sa najvećim protokom helijuma od 32 l/min imali su najbolju mikrostrukturu i mehaničke karakteristike. Kroz slojeve prevlaka uočavaju se fine mikropore bez prisustva grubih pora, što je u skladu sa mehaničkim karakteristikama slojeva. U mikrostrukturi nisu prisutne nestopljene čestice praha. U deponovanom stanju čestice praha WC-12tež.%Co su dobro istopljene i međusobno povezane i prave kontinualne i neprekidne slojeve prevlake. Zbog razlaganja primarnog karbida WC, koje se ne može izbeći u procesu depozicije, prevlaka pokazuje višefaznu mikrostrukturu. U mikrostrukturi su prisutna zrna uglastog oblika nerazgrađenog primarnog karbida WC. Razlaganjem primarnog karbida WC zrna se zaobljavaju po ivicama. Formirani karbid W_2C izdvaja se u obliku globula po ivicama ili površini primarnih zrna karbida WC. Neka primarna zrna WC karbida mogu biti potpuno okružena W_2C karbidom (tačka 3). Primarni karbid WC je tamnosive boje, a W_2C karbid svetlo- bele boje (Li, et al., 1996, p.785), (Verdon, et al., 1998, p.11). U mikrostrukturi su prisutne tri kristalne faze WC, W_2C i W rastvoren u osnovi veziva Co. Kao posledica reakcija razlaganja, nešto ugljenika C rastvara se u osnovi Co, a nešto reaguje sa kiseonikom formirajući CO/CO_2, čime se gubi deo ugljenika C iz polaznog praha. Zadržani C u osnovi Co sa W obogaćuje osnovu Co (He, Schoenung, 2002, pp.274-319), (Verdon, et al., *1998, pp.11-24). U zavisnosti od stepena dekarburizacije, metalni W može da se taloži blizu granica lamela (Qiao, et al., 2003, pp.24-41).*

Zaključak

Atmosferskim plazma-sprej postupkom (APS) deponovane su WC-12tež.%Co prevlake sa tri protoka helijuma 8 l/min, 16 l/min i 32 l/min. Analizirane su mehaničke i mikrostrukture osobine deponovanih prevlaka na osnovu čega se došlo do određenih zaključaka.

Mehaničke osobine i mikrostrukture WC-12tež.%Co prevlaka bile su u direktnoj zavisnosti od protoka plazma-gasa helijuma. Sa povećanjem protoka helijuma doponovale su se prevlake sa većim vrednostima mikrotvrdoće i zatezne čvrstoće spoja. Prevlaka deponovana sa najvećim protokom helijuma od 32 l/min imala je 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 bile su u skladu sa njihovim mikrostrukturama.

U mikrostrukturi prevlaka prisutne su pore crne boje. Pore su bile najmanje izražene u slojevima prevlake deponovane sa protokom helijuma od 32 l/min. U tim slojevima prisutne su fine mikropore bez prisustva grubih pora, što je u skladu sa mehaničkim karakteristikama i mikrostrukturom slojeva. Najizraženije i najgrublje mikropore imali su slojevi deponovani sa protokom helijuma od 8 l/min.

U mikrostrukturi su prisutne kristalne faze WC, W_2C i W koji je sa C rastvoren zajedno u osnovi veziva Co. Rastvoreni W sa C u osnovi veziva Co, obogaćuje osnovu Co. Prevlaka deponovana sa protokom helijuma od 32 l/min pokazala je najbolje mehaničke karakteristike i mikrostrukturu.

Ključne reči: *plazma, mikrostrukture, mehanička svojstva, slojevi, protok gasa brzina toka, prevlaka, Co.*

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