BALKANTRIB'O5
5th INTERNATIONAL CONFERENCE ON TRIBOLOGY
JUNE.15-18. 2005
Kragujevac, Serbia and Montenegro

PLASMA SRAYING OF CARBIDES BASED COMPOSITES USING NEW PLASMA TORCH DESIGN

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Abstract
This paper demonstrated the possibility of depositing good quality WC/Co and Cr_3C_2 /NiCr coatings by using the PJ-100 plasma torch of a novel design. The hardness and adhesion strength of the carbide based coatings obtained in this investigation are compared with the values obtained by conventional plasma torch and the HVOF spraying. The good qualities of carbides coatings attained by PJ-100 plasma installation are results of a longer plasma plume with homogeneous temperature profile and much higher plasma speed.

Key words: *Plasma spraying, karbide coatings, plasma gun*

INTRODUCTION

Thermal spraying technology has been widely used for reparation as well as for the surface enhancing of parts for theirs first assembling. The metal-ceramic composites based on wolfram and chromium carbides are technologically important abrasive and sliding wear resistant coatings. The WC/Co and Cr_3C_2/NiCr and composites, either solo or in combinations are most frequently in use, and those in combination are considered as a good replacement for hard chroming coatings [1]. In comparison with the hard chroming technology, plasma spraying of the composites offers several important advantages such as: the possibility of applying the thick coating, the higher coating speed, there is no limitation regarding the substrate materials on which the coating applies, there is no bulkiness constrains for the coated substrate, and the plasma spraying is less hazardous ecologically and environmentally than hard chroming. Also, due to the higher stability of the hardness with the rising temperature, the carbide based coatings are preferable for the high temperature applications. The maximum working temperature for the hard chromium is 400^{o}C while the hardness begins to drop already from 200^{o}C. The WC/Co is usable up to 550^{o}C while the Cr_3C_2/NiCr coating is usable up to 950^{o}C [1] and its hardness considerable drops at temperatures over 600^{o}C [2].

Among the existing techniques of thermal spraying the plasma coating is most flexible and, because of high temperature plasma plume, has no constraints regarding the materials that can be melted. In case of the coating of oxide ceramics with the hardness up to 2400HV the plasma spraying has no rivalry. However, for the coatings based on the carbides ceramics the high temperature of plasma plume is considered as a serious limitation because of thermal decomposition of carbide at approx 3000K. Therefore, the technology of choice for the spraying of carbides based coatings is the High Velocity Oxygen Fuel (HVOF), where the flame temperature is nearly four times lower than the temperature of the dc-arc jet.

This paper presents the results achieved in plasma spraying of WC/Co and Cr_3C_2/NiCr with the novel construction of dc-arc plasma gun. The new gun construction with the power level of 100kW generates the plum with advanced plasma characteristics if compared with the existing conventional torch designs. This new construction allows a different and specific approach to the plasma spraying of carbides based materials and it is discussed in this paper.

EXPERIMENTAL METHODS

The plasma spraying was done in APS mode with the PJ-100 plasma jet installation (produced by *Plasma Jet Co*, *S&MN*) powered at 100kW [3]. For the spraying of the wolfram carbide cermets coating the W_2C/WC 12Co composition and the particle sizes range 45 - 75μm (the 71 NS quality) was used. In the case of the chromium carbide cermets coatings the Cr_3C_2 25Ni 5Cr powder of two particle sizes ranges; 11-106μm (81 NS) and 5 - 45μm (81 VF) were used. All powders are produced by Sulzer Metco, USA. The plasma gas was Argon and Hydrogen mixture. The gun's working parameters are given in Table I

Table I PJ-100 gun's working parameters

Argon flow rate	70 – 121 l/min
Hydrogen flow rate	27 - 44 l/min
Voltage	185 – 190 V
Amperage	420 – 450 A
Power	80 – 90 kW

The 60 x 15 x 2mm steel plates and tensile test specimens of the same material were the substrates for coating. Plates and tensile test specimens were mounted on a rotating disk and the spraying was done perpendicularly on the disk surface. The disk's rotation speed was chosen to give a linear speed of 0.5 – 1 m/sec in the sections where the substrates were mounted, while the torch translation velocity was 0.5 – 1 m/min.

The adhesion force of the coating to the substrate was tested on mechanical testing machine Instron 1185 with a bridge velocity of 1mm/min. The tensile test specimens 25.4mm in diameter are paired with a mismatch less than 0.01mm, in accordance to the ASTM C 633-79 standard. The gluing of the tensile test specimens was done with one component epoxy glue "Klebbi" (Sulzer Metco). Polymerization of the glue was done at 180°C for two hours. According to the glue producer specification, the limit for the glue/holding strength is about 100 MPa, while our measurements show that this value is 83.6 ± 5.2 MPa. The hardness of the coating was determined by macro-hardness (HV50) testing.

The microstructure characterization of deposited layers was done by Zeiss Axiovert light microscopy. The X-ray diffraction analysis (XRD) was used for evaluation of the phase changes of powders brought about by plasma spraying. The XRD analysis was done on the Siemens D500 diffractometer with CuKα radiation. The voltage and current intensity on the X-ray tube were 35kV and 20mA, respectively.

RESULTS AND DISCUSSION

The PJ-100 plasma torch produces a plasma plume length of 60 – 70mm, which is more than twice of the plasma plume length generated by standard dc-arc plasma guns. The design of the PJ-100 [3] allows the cathode tip and the bottom of the anode nozzle are to be physically separated by predetermined gauge, so that the arc path from cathode to anode exit is collinear with the gas flow. It enables an excellent heat transfer from the arc to the gas facilitating on that way the formation of the plasma plume with far more homogeneous temperature across the plume diameter than it is with the conventional dc-arc plasma torch. In addition, the PJ-100 plasma plume posses approximately twice of the power the conventional plasma torch has, with much higher thrust. These technical and physical plasma characteristics of this novel plasma torch design are reported elsewhere [3].

The main role of plasma plume in plasma spraying process is to supply to the powders material introduced into plasma jet, with enough heat to melt it down and to accelerate them toward the substrate. For the carbide powders injected into the plasma jet a specific - moderate - approach to the spraying parameters is required to preclude an excessive heating of carbides particles. The following engineering logic is used in our approach to overcome the carbide thermal instability at higher temperature of the dc-arc plasma. We used the available high power capacity of the plasma plume of the PJ-100 plasma torch and injected in the plasma jet much higher mass of powder materials. And this approach has shown to be advantageous in case of carbide based coating systems. Based on this energetic principle, higher mass input of materials decreases the temperature at which the particles were heated while traveled with the plasma jet. Therefore, the coating was conducted with the mass input in the range of 14 – 24 kg/h for the WC composite, and 8.0 – 17.3 kg/h, for coarser Cr_3C_2 and 10.0 – 20.2 kg/h for finer Cr_3C_2, composite.

WC/Co coating

The plasma spraying of WC/Co due to early start of thermal decomposition of WC which is well below 3000K [4], is temperature sensitive process, and hence a considerable correction of spraying parameters was required. Firstly, Hydrogen presence in the plasma gas which is, otherwise, very beneficial for the work of plasma torch had to be restricted at the lower possible level. It is required because Hydrogen is reacting with the carbon released by dissociation of WC particle producing the CH_4 gas which increases the porosity of deposited coating. Additionally, an increased content of Hydrogen in plasma gas would increase the thermal conductivity of plasma what is unfavorable in case of carbides coatings. The ordinarily used process to cooling the melted particles by injection of a cool gas (usually air) into plasma plume; so called jet crossing, is not practical here because an excessive oxidation of liberated carbon to CO_2 would occur, and also a direct reaction of WC oxidation would be possible. Therefore for WC/Co spraying the lowest Hydrogen content in Argon was chosen, and coating was done without additional cooling by air injection. Distance between the substrate and torch nozzle from which the spraying was done was changing from 100 to 300mm. Microphotographs of deposited layer sprayed from 100mm and 300mm distance are shown in Fig1.

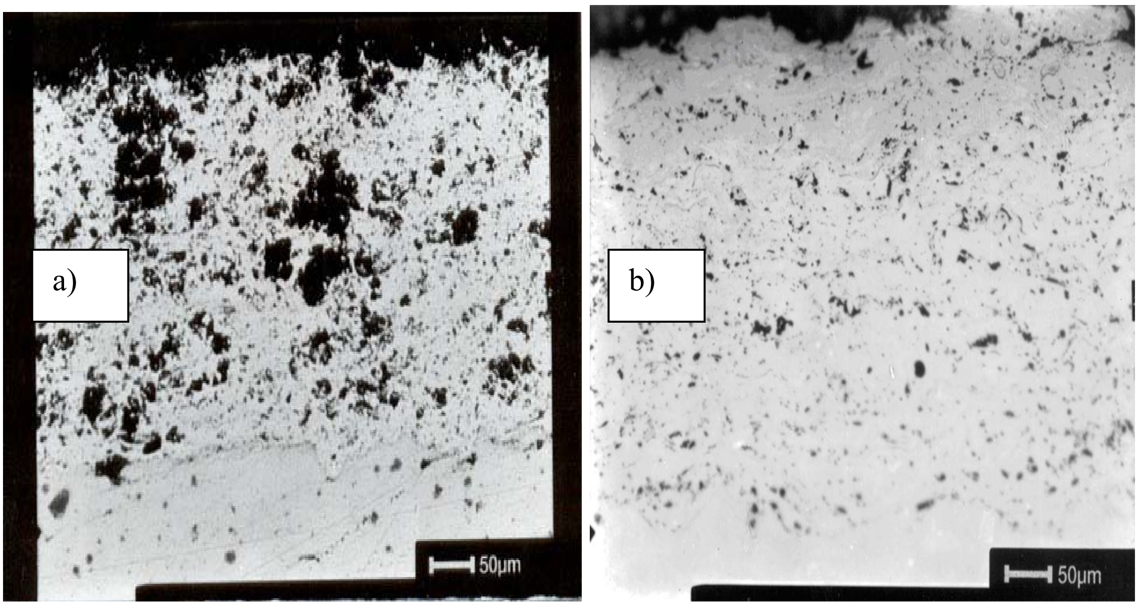

Fig. 1: *Microphotographs of the layer sprayed with 71 NS from different distances: 100 mm a), and 300 mm b).*

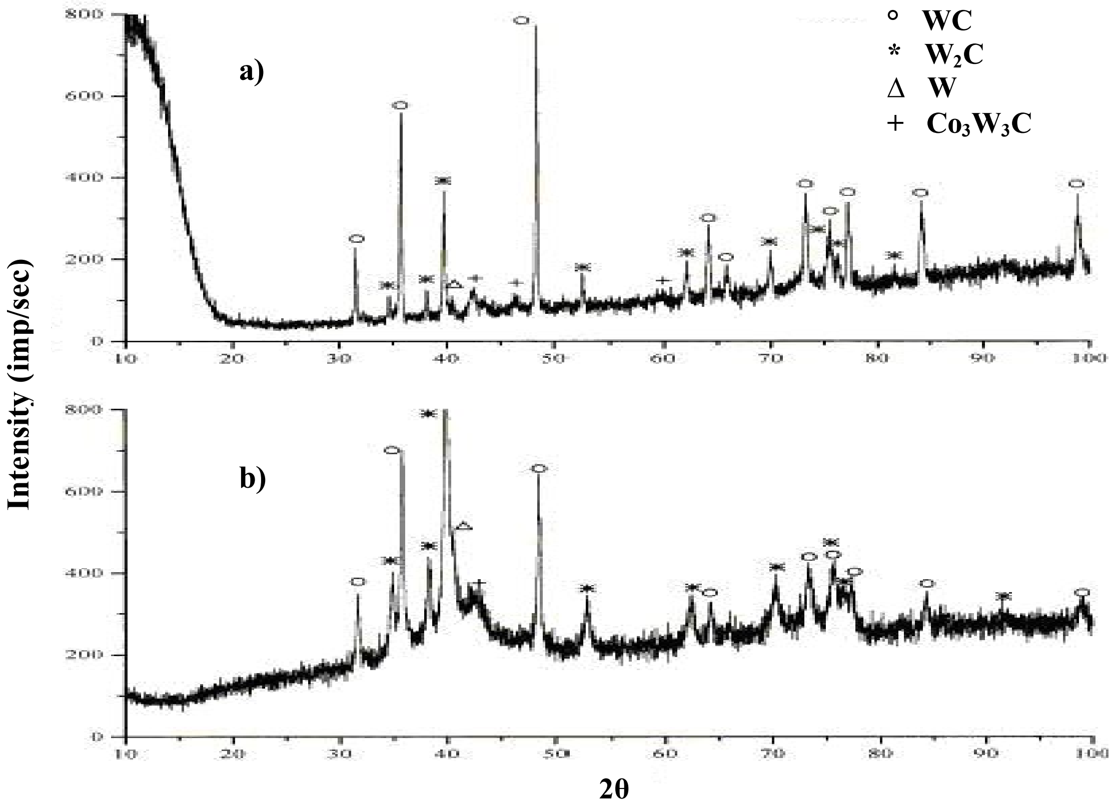

Fig. 2: *Diffractograms of the 71 NS powder (a) and the coating sprayed by dc-arc plasma (b)*

Much higher porosity is apparent for the coating sprayed from distance of 100 mm. The cause for this higher porosity are gases liberated from excesively heated particles embodied in the deposited layer. In case of plasma spraying from distance of 300 mm the gas liberation in the deposited layer is gretaly subdued due to the cooling of the particles on theirs three times longer flying distance.

Fig. 2 shows the X-ray difractograms of the 71 NS powder and the sprayed coating. Besides the WC and W_2C diffractions thera are diffraction lines for metal Wolframe and for the compex Co_3W_3C - **η** phase. Difractions of pure Cobalt were not detected. By comparing the diffractions of the 71 NS powder and the sprayed coating, it can be concluded that during the melting and subsequent deposition process a part of WC decomposes to W_2C, during the cooling process. It is substantiated by increased fraction of W_2C found in deposited coating. The fraction of the brittle **η** phase in the coating rises too. The broadened amorphous diffraction at the 2θ from 40 to 46^o is taken as a proof for the presence of complex Co-W-C carbides. At the same time the content of free non reacted Wolfram increased. With the chosen plasma generation parameters an acceptable degree of WC decomposition has been attained. The strong diffractions of WC in the coating and the absence of the free carbon peak, which would appear at 26.59 in the case of a greater decomposed fraction of WC/W_2C, is taken as the proof that the greater part of WC stays unchanged.

Decomposition of the WC cannot be precluded totally even during the spraying by HVOF method, which plume has much lower temperature. This was shown elsewhere on the examples of deposition of five different types of WC/Co powders [4]. Powder 71 NS used for coating in our investigation already contained brittle **η** phase and undetected amount of Cobalt, and both these features are unfavorable for the formation of a sound coating. A good WC/Co coating is near to the quality of sintered WC/Co cermets i.e., would preserve the presence of Cobalt phase and prevent the formation of brittle **η** phase, what is still unachievable with the existing thermal spraying methods. The noticeable result of investigation of the WC/Co coating conducted in this study is that good quality of coating was achieved by spraying from distance of 300mm. This is considerably longer distance than usually applied by the APS spraying; it's the distance which is common for the low pressure plasma spraying (LPPS). It was possible with Pj-100 torch to spray from much longer distance because of much higher plasma velocity and thrust, as well as twice longer plasma plume that all enable very efficient momentum transfer from plasma to the melting particles.

Cr_3C_2/NiCr coating

The chromium carbide phase is far more stable than WC allowing flexibility in choosing the spraying parameters. The equally good quality of coating was achieved by applying "jet crossing" cooling when the spraying was done from distance of 100mm and by spraying from distance of 200mm without subsequent cooling.

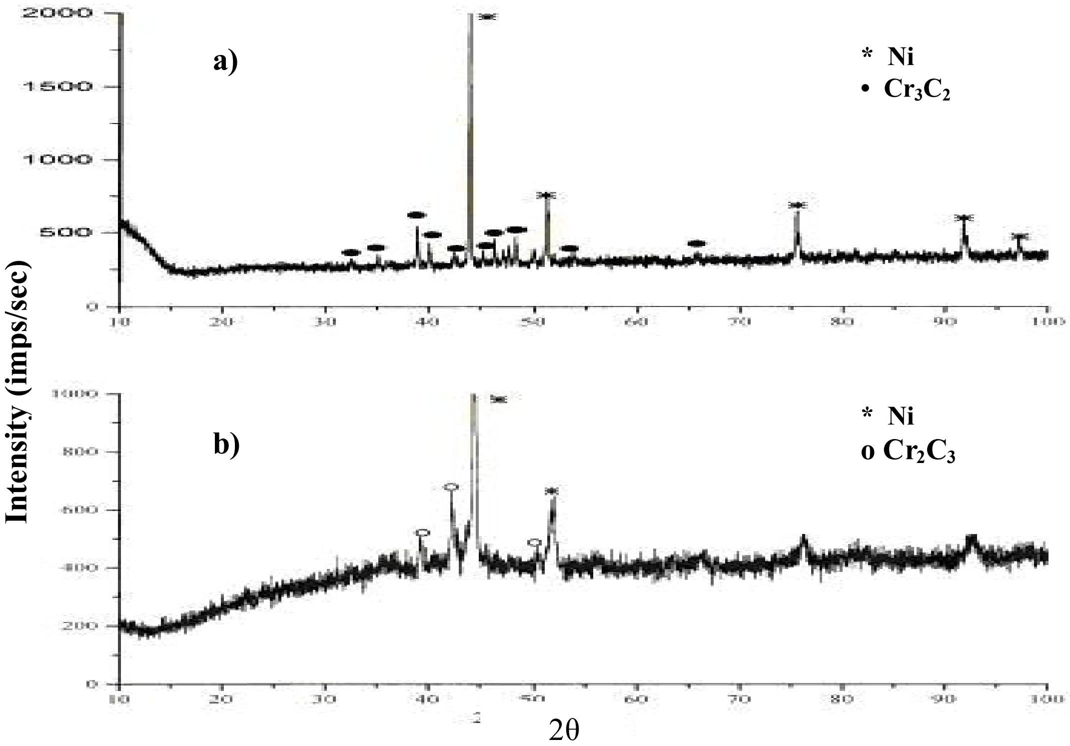

Fig. 3: *Diffractograms of 81 NS powder (a) and the coating sprayed by dc-arc plasma (b)*

Fig. 3 shows the characteristic diffractions of the 81NS powder and deposited coating. Nickel and Cr_3C_2 were detected in the powder, and Cr_7C_3 as dominant phase in the coating. The appearance of strong Cr_7C_3 diffraction, related to the equilibrium Cr – C phase diagram [5], shows that cooling of the liquid particles proceeded under non-equilibrium conditions. On other words, as the powder goes trough melting and solidification the partial decomposition of Cr_3C_2 takes place, and the Cr_7C_3 precipitation from the liquid phase is taken as the proof for such decomposition. The Nickel is much less potent carbide former than Cr, meaning that there is no any substantial replacement of chromium by nickel in the carbide phase (the absence of the $(Cr,Ni)_7C_3$ and $(Cr,Ni)_{23}C$). This retention of the Ni metal phase in the coating explains the good adhesion of the 81NS coating to the substrate material.

Microphotographs of coatings sprayed with 81 NS and 81 VF powders are shown in Fig. 4. The fine grained structure is apparent in case of spraying with the finer powders.

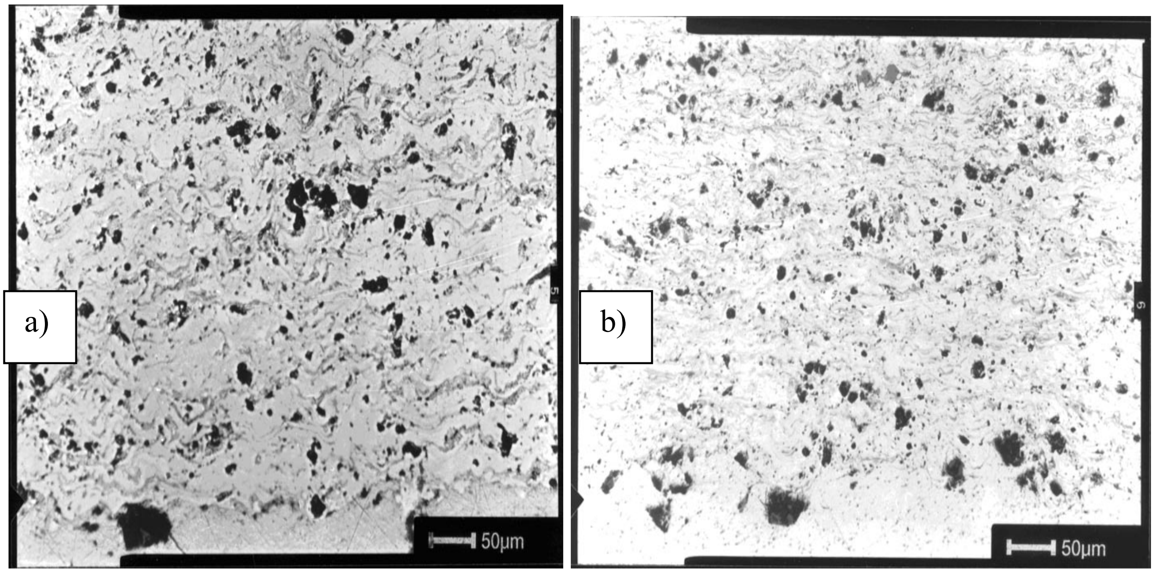

Fig. 4: *Microphotograph of cross section of Cr_3C_2/20Ni 5Cr coatings: a) 81 NS powder; 2.4 g/s and b) 81 VF powder; 2.8g/s, and plasma power of 80 kW.*

The values of macro-hardness (HV50) and adhesion of deposited coatings to the substrate are presented in Table II. The given values are averaged in the interval between the lowest and highest measured value for each quality of coating.

Table 2. Hardness and adhesion of wolfram and chromium carbide based coatings

Powder	HV50	Adhesion, MPa
71 NS	976±38	41.4±4.0 49.6±9.5
81 NS	782±168	52.9±7.1 72.2±1.0
81 VF	852±105	52.4±7.0 63.4±6.6

The results in Table II show that the cermets coatings sprayed by the PJ-100 plasma installation are of very good quality. Values for the hardness of wolfram and chromium carbides based coatings sprayed with PJ-100 torch are compared with the Sulzer Metco certified values (40-45 HRc,) for the coatings obtainable with the same powders we used. The hardness of our coatings shows an significant increase. This significant difference is not unexpected because the conventional dc-arc plasma spraying installations work with the lower plasma power. It should be emphasized however, that these big differences in achieved hardness is not just because of different plasma power applied but because of the differences in plasma characteristics of these two different plasma torch designs [3]. Hardness and adhesion data for the Cr_3C_2 /NiCr coating sprayed with conventional plasma installation (35kW and powder input of 2.28-2.52 kg/h) reported by Plasma Technik [6]. is 400(HV) and 34.5MPa, respectively. It is also interesting to compare the hardness and adhesions values obtained by spraying with PJ-100 with the results reported for the coatings obtained with HVOF spraying. For the WC/Co cermets coating with specially prepared WC 17Co powder sprayed by an improved High Thrust HVOF spraying method the hardness value of 1048±68 (HV0.3) and adhesion of 73MPa were reposted [7]. The results of another study of HVOF spraying [2] with four different Cr_3C_2 /NiCr powders of different granulation (obtained by differently methods; blending and agglomeration) are not directly comparable with the 81 NS powder (Metco's blended carbide with metal fraction) we used in our study. For those four different

Cr_3C_2 /NiCr powders, the authors [2] obtained 400-890 HV for hardness and the 55 – 80MPa for adhesion. For the finer granulation (5 - 35μm) which is comparable with 81 NS we used they obtained the hardness of 700±40HV and adhesion of 75MPa. It is apparent that the hardness and adhesion for chromium carbide cermets sprayed by JP-100 plasma torch is very close to the values achieved by HVOF. However, the employed powder feeding rate during HVOF spraying of Cr_3C_2 /NiCr was 1.8 – 2.4 kg/h [5] what is one magnitude lower rate than in our plasma spraying.

Another interesting notion can be discerned when the values in Table II and microstructure of corresponding coatings are compared for Cr_3C_2 /NiCr coatings. The spraying of finer granulation (81 VF) gives considerably finer microstructure which has an effect on higher hardness values and narrower distribution of measured values. However the hardness difference between tested granulation is not significant, while the adhesion is the same for both granulation, and even a bit better for the coarser granulation. The reason for this is an unfavorable influence that the high temperature and total plasma plume energy have on the finer powder fraction injected into plasma jet. The finer powder is overheated and probably went through higher burn out than the coarser. On other side, due to the considerably longer plasma plume, the transfer of velocity from plasma jet to the particles is more efficient even for the coarser particles. The smaller particles are probably accelerated to the higher velocities. However, because of their smaller mass they have no larger kinetic energy than coarser ones. The results obtained in the conducted study of plasma spraying of chromium and wolfram carbides cermets reveal the potentiality that plasma plume generated by PJ-100 torch has for the quality improvements of thermally sprayed coatings. It allows the plasma plume to be loaded with a higher input of injected powders what is decisive for good quality of carbide cermets coatings obtained in this study.

CONCLUSIONS

This paper demonstrated the possibility of spraying the good quality Cr_3C_2 /NiCr and WC/Co coatings by using a novel design of plasma torch.

The attained qualities of coatings with PJ-100 plasma torch are excelling the qualities attained by existing conventional spraying plasma torch constructions. The values for hardness and adhesion measured on coatings sprayed with JP-100 plasma gun are close to the values measured on the coatings deposited with HVOF method. As a bonus, the plasma jet coating with PJ-100 installation enables ten times greater mass input into plasma jet, what is a big cost advantage for a thermal spraying technology. The conducted investigation revealed the need for further optimization of the plasma spraying process both in terms of the granular size and the powder composition. It is particularly evident for the WC based coatings for which, even better results could be attainable by adjustment the plasma plume characteristics, primarily by finding an appropriate gas mixture and flow rate.

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