

Improving the Wear Resistance of Thermally Sprayed Nanocomposite Cr₃C₂-25NiCr Coatings by Pulsed Plasma TreatmentM.G. Kovaleva^{1,*}, V.V. Sirota², V.M. Beresnev³, Yu.N. Tyurin⁴, O.N. Vagina¹, I.A. Pavlenko¹¹ Belgorod National Research University, 85, Pobedy Str., 308015 Belgorod, Russia² Belgorod State Technological University named after V.G. Shoukhov, 46, Kostyukov Str., 308012 Belgorod, Russia³ V.N. Karazin Kharkiv National University, 4, Svobody Sq., 61000 Kharkiv, Ukraine⁴ E.O. Paton Electric Welding Institute, NASU, 11, Bozhenko Str., 03650 Kyiv, Ukraine

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In this study the surfaces of thermally sprayed nanocomposite Cr₃C₂-25NiCr coating have been treated by the pulsed plasma. The nanocomposite Cr₃C₂-25NiCr coating was deposited by a new multi-chamber gas-dynamic accelerator on grit blasted steel substrate. An automatic pulse-plasma device "Impulse-6" was employed to plasma treatment the surface of Cr₃C₂-25NiCr coating. The microstructure and wear resistance of the surface of the nanocomposite Cr₃C₂-NiCr coating before and after the pulsed plasma treatment (PPT) was studied in this paper. Wear tests were carried out using a computer controlled pin-on-disc type tribometer at 25 °C. The specific wear rate of the nanocomposite Cr₃C₂-25NiCr coating after PPT is approximately four times less than that of the Cr₃C₂-25NiCr coating before PPT, indicating that the nanocomposite Cr₃C₂-25NiCr coating after PPT exhibits better wear resistance. Detailed analysis indicates that the enhanced wear resistance of the nanocomposite Cr₃C₂-25NiCr coating after PPT is mainly attributed to the formation of an oxide tribolayer and smoother surface, which result from the dense and amorphous microstructure of the coating.

Keywords: Hardmetal coating, Chromium carbide, Multi-chamber gas-dynamic accelerator, Pulsed plasma treatment, Wear resistance.

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1. INTRODUCTION

Cr₃C₂-NiCr material based on hard carbides embedded in a metallic matrix (Cr₃C₂-NiCr system) is widely used to apply wear, erosion and corrosion protective coatings for various kinds of industrial applications [1-4]. Cr₃C₂-NiCr cermet coatings are deposited by the various thermal spray coating processes such as high velocity oxy fuel (HVOF), cold-spray, detonation gun spray, atmospheric plasma spraying and other [2, 5-7]. However, the coatings prepared by these methods have several drawbacks: low hardness and wear resistance of the surface of coating, the existence of pores in the coating (from 0.5 % to 1.8 %) [4], which cannot meet the demand for long service life of the workpiece. To improve these properties, various methods have been proposed, such as post heat treatment, seal sintering with liquid alloys, impregnation with polymers or ceramics, post-laser irradiation, sparking plasma sintering and pulsed plasma treatment [4, 8-10]. The influence of pulsed plasma treatment on the wear resistance of nanocomposite Cr₃C₂-25NiCr coatings was studied in this paper, in order to provide a reliable basis for the practical application.

2. EXPERIMENTAL PROCEDURE

In our previously work [14] the Cr₃C₂-25NiCr powder (POLEMA JSC, Russia; d(0.1): 35.57 μm, d(0.5): 78.3 μm, d(0.9) : 141.72 μm) was used to obtain hardmetal coatings on steel substrate (Fe ~ 67 Cr ~ 17-19 Ni ~ 9-11 Cu ~ 0.3 Mn ~ 2 C ~ 0.12, all in wt %) by a new a multi chamber gas-dynamic accelerator (MCDS) [15]. In the present study, an automatic pulse-plasma device

"Impulse-6" [13] was employed to treatment the surface of nanocomposite Cr₃C₂-25NiCr coatings at following conditions: capacity of the capacitor bank – 960 μF; voltage on the plates of the capacitor bank – 3.2 kV; inductance of the discharge circuit – 30 μF; deepening electrode – 20 mm; distance from the sample – 40 mm; velocity of the plasma torch – 5.5 m/s; pulse repetition frequency – 1.5-2 Hz. The surface is treated with the pulsed, electric, magnetic, acoustic and elastic-deformation fields, thus enhancing the "abnormal" heat and mass transfer processes and providing formation of new materials and alloys in surface layer [13].

The obtained specimens were transversally cut by spark erosion mechanically polished and, prepared by standard metallographic sample preparation sectioning, mounting and polishing methods. This involved grinding with abrasive SiC paper. The specimens were then polished using 6, 3 and 1-micron diamond polishes on a lubricated cloth. To determine the microstructure and elemental composition of the sample surface scanning electronic microscopes (SEM) Quanta 200 3D was performed. Phase composition of the samples was determined by the X-ray phase analysis method (diffractometer ARL XTRA). The tribological evaluations of the coated substrates under dry conditions were performed using a ball-on-disc tribometer CSM Instruments according to ASTM G-99. The ASTM G-99 standard determines the amount of wear by measuring the appropriate linear dimensions of both specimens (ball and disk) before and after the test. During testing the friction coefficient was recorded as a function of the sliding distance. Tests were performed at ~ 25 °C and ~ 60 % relative humidity. A 6 mm in diameter Al₂O₃ ball was

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used as a counter body. Specimens were tested under a 6N normal load, a radius of the wear circle of 5 mm, a $0.15 \text{ m}\cdot\text{s}^{-1}$ sliding speed and a total sliding distance of 1200 m according to ASTM wear testing standard G-99. The total wear volume was calculated by measuring the track cross-sectional area with a stylus profilometer (Taylor-Hobson) at ten different locations along the wear track. The roughness (Ra) of the surface coatings before wear testing was measured by a Taylor-Hobson Surtronic 25 profilometer. The all obtained samples are characterized by almost the same microstructures and wear resistance. Arbitrary selected data are presented in the paper.

3. RESULTS AND DISCUSSION

The microstructure of the coating cross section is shown in Fig. 1. The plasma-modified outer layer does not possess microcracks or pores (Fig. 1, point 1). The thickness of the modified layer was 2-5 microns. No peeling of the coating was observed after plasma treatment. As a result of the pulsed plasma treatment the composition of the surface of nanocomposite Cr_3C_2 -25NiCr coatings is changing. Chemical effect on the surface of coating is realized due to an addition to plasma of the materials (W, C, N) that initiate or accelerate chemical reactions (catalysts) and enter into chemical interaction with the materials of coating sur-

face [10]. The coating structure significantly varies with depth. There are dark plasma-modified outer layer on the top (Fig. 1, point 1). Pulsed metal-gas plasma processing can be applied for doping of melted layer with plasma brought atoms [14]. A microanalysis of this region revealed the presence of W and Fe. We assume that presence of wolfram atoms in surface coating was due to its presence in the pulse-plasma device gas atmosphere and the result of synthesis eroding electrode, since distribution of W atoms over the coating depth and width shows uniform character. It is believed that Fe penetrates from the substrate as a result of dynamic and temperature action of the plasma jet.

Fig. 2a shows SEM images of the surface of a coating that was not additionally treated by the plasma jet. The surface shows a typical relief: a high roughness results from the presence of powder particles deformed by dynamic impact and fusion in the plasma jet. The roughness parameters Ra of the coating surface after deposition was $10.51 \pm 0.01 \mu\text{m}$; after plasma treatment it decreased down to $7.26 \pm 0.01 \mu\text{m}$. The peaks of relief before plasma treatment are apparently hard alloy particles. The additional treatment of the coating surface by the plasma jet yielded no powder particles on it (Fig. 2b). Powder particles or fragments rising above the surface are melt and the surface roughness declines by $\approx 30 \%$.

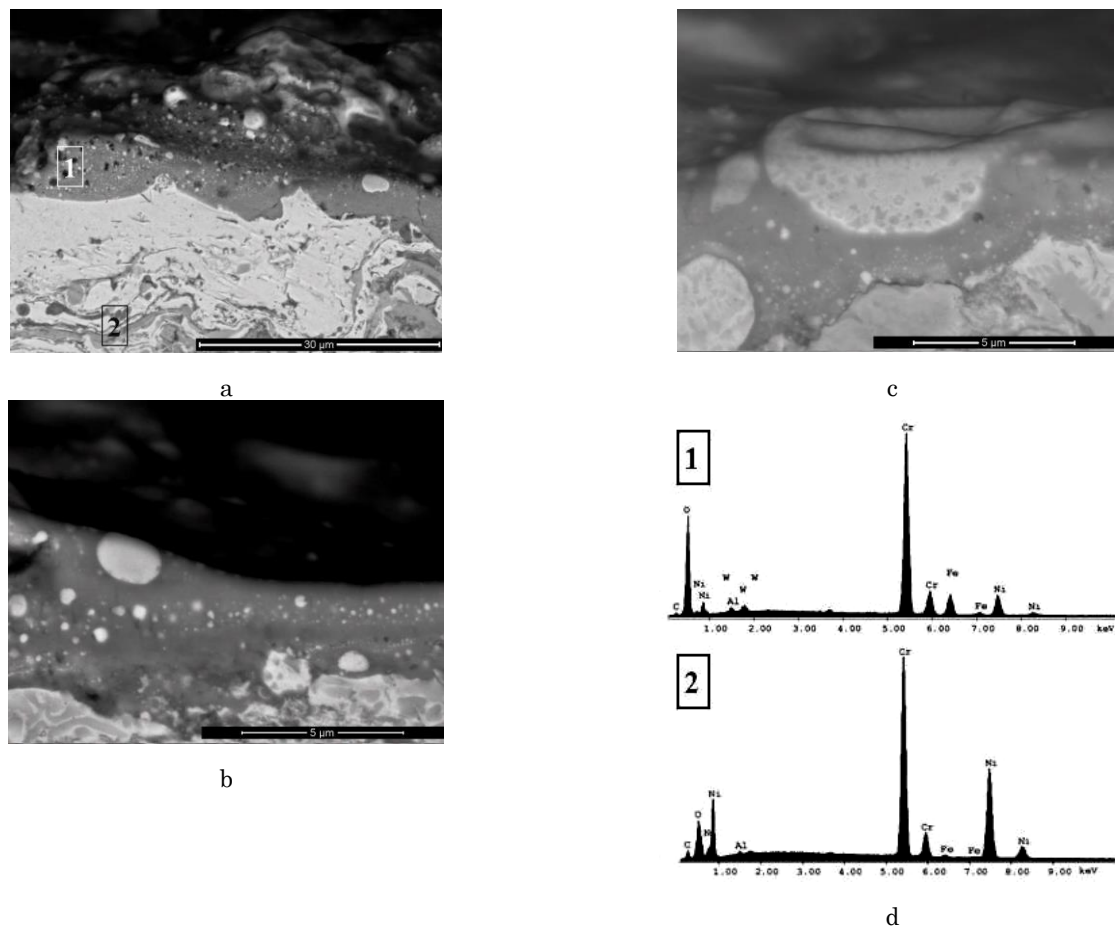


Fig. 1 – SEM BSE micrographs (a-c) and elemental composition (d) of the coating layer after plasma treatment

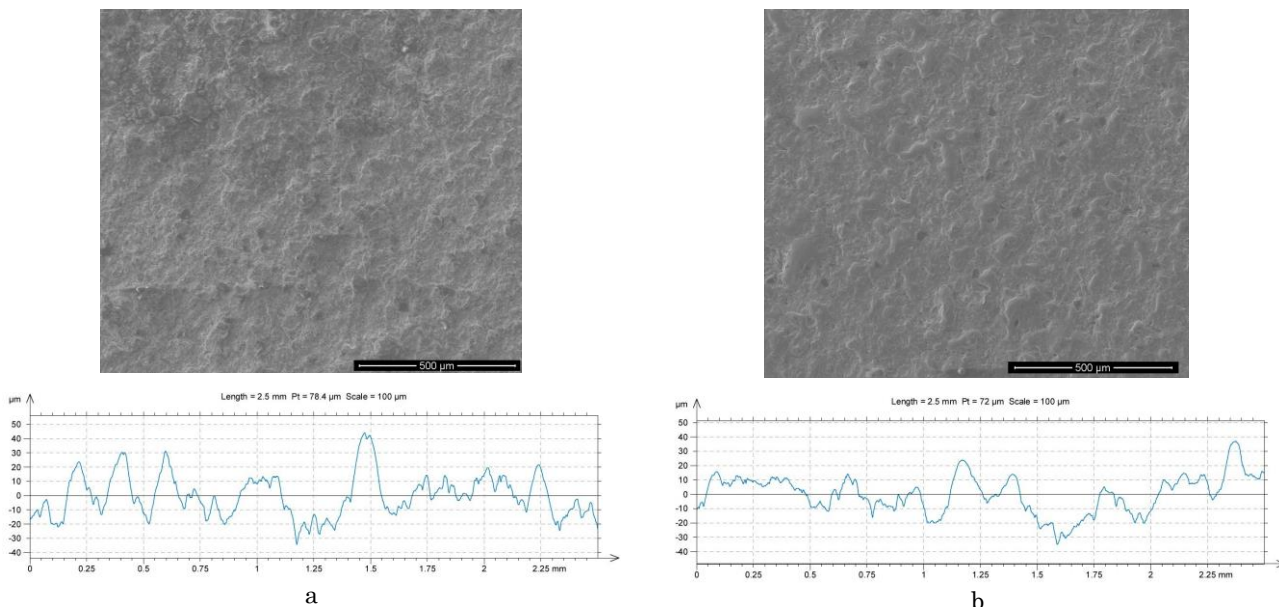


Fig. 2 – SEM images and surface microgeometry of portion of the surface of coating before (a) and after plasma treatment (b)

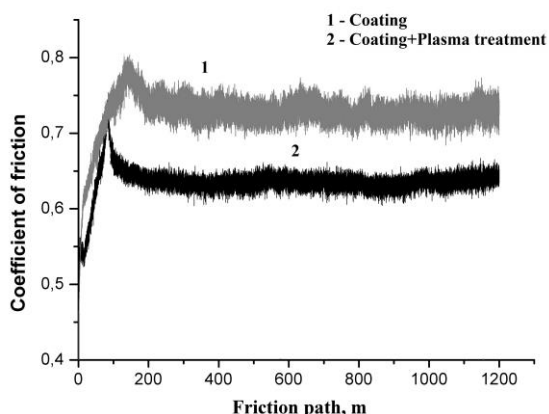


Fig. 3 – Friction coefficient as a function of sliding distance

The graph (Fig. 3) refers to the tests on nanocomposite $\text{Cr}_3\text{C}_2\text{-}25\text{NiCr}$ coating before and after modification by plasma treatment. An exemplary graph shows the friction coefficient profiles as a function of sliding distance for the load of 6 N (Fig. 3).

Increasing wear resistance is achieved for samples with $\text{Cr}_3\text{C}_2\text{-}25\text{NiCr}$ coating subsequent pulsed plasma treatment (Table 1). It was found that the average friction coefficient (0.73) of nanocomposite $\text{Cr}_3\text{C}_2\text{-}25\text{NiCr}$ coating is higher than the friction coefficient (0.64) of $\text{Cr}_3\text{C}_2\text{-}25\text{NiCr}$ coating after plasma treatment (Fig. 3). It effect might be produced due to the elimination of surface defects (microcracks and pores) and changes in the structural-phase state of the coating (Fig. 4). The XRD patterns of the surface of coating before plasma treatment are shown in Fig. 4a and Table 1.

Table 1 – The phase composition and results of the investigation of nanocomposite coatings $\text{Cr}_3\text{C}_2\text{-}25\text{NiCr}$ before and after pulsed plasma treatment

Sample	Identified major phases	Surface roughness (not polished surface) $R_a \pm 0.01$ (μm)	Specific wear rate ($\times 10^{-5}$) ($\text{mm}^3(\text{m}\cdot\text{N})^{-1}$)
Before plasma treatment	Cr_2C , Cr_7C_3 , Ni-Cr-Fe , $\text{Ni-Cr-Fe/Cr}_7\text{C}_3$	10.51	8.53
After plasma treatment	Cr_2O_3 , Cr_2C , Ni-Cr-Fe , $\text{Ni-Cr-Fe/Cr}_7\text{C}_3/\text{Cr}_2\text{O}_3$	7.26	2.06

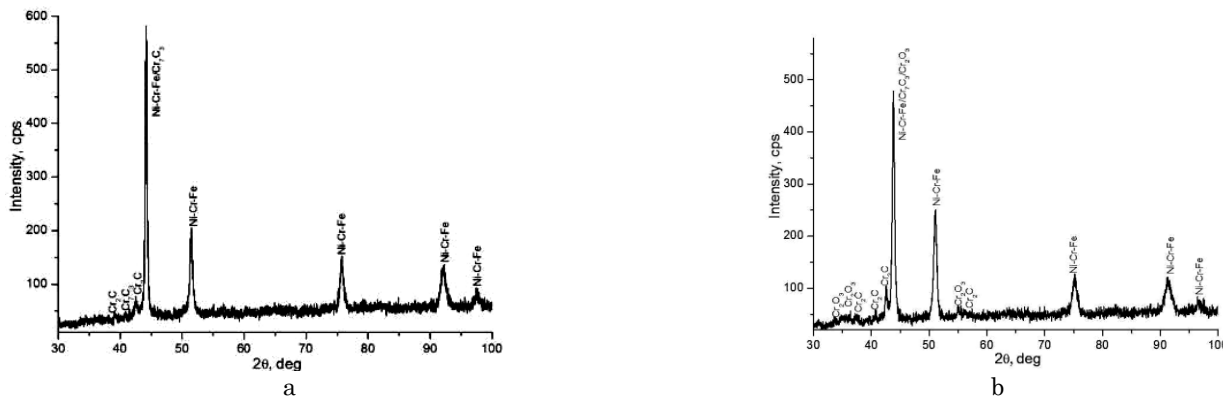


Fig. 4 – XRD patterns of the coating layer before (a) and after (b) plasma treatment

The detected phases were Ni-Cr-Fe, Cr₂C and Cr₇C₃ phases (Fig. 4a). It can be seen that no peaks corresponding to metallic oxides were detected in nanocomposite Cr₃C₂-25NiCr coating before plasma treatment. After treatment of the coating surface by pulsed plasma jet the near surface region also was composed of Ni-Cr-Fe and Cr₂C phases. As for the Cr₇C₃ phase, it was at the lowest limit of detection (< 5 volume %). As a result of treatment in the coating, the content of carbide Cr₂C increases and the content of Ni-Cr-Fe decreases as a result of oxidation and the formation of oxides. After the coating modification, oxide Cr₂O₃ is formed on the surface. X-ray analysis confirmed that thermal activation of a surface by pulsed plasma jet provided saturation of near surface coating layer by oxide compounds. All peaks of nickel solid solution and chromium carbides become broad, and a very broad peak centered around 43° appears. The very broad peak indicates formation of an amorphous phase. Therefore, it is considered that nickel-chromium alloy and some carbide are melted and some amorphous phase forms.

CONCLUSIONS

A pulsed plasma treatment can be effective in modifying the state of the outer layer of Cr₃C₂-25NiCr

coatings and thus can modify their functional properties. The provided experiments have shown evidences that the Cr₃C₂-25NiCr coatings with plasma treated surface were more resistant to wear than as-sprayed Cr₃C₂-25NiCr coatings. After the coating modification, oxide Cr₂O₃ is formed on the surface and the content of carbide Cr₂C increases. Chromium oxide is a high hardness ceramic material and it is widely used in coatings for its excellent tribological properties such as high wear resistance. Hard carbides and oxide of Cr distribute uniformly in the outer layer of coating and have a high bonding strength with the matrix, which can heighten the coating's resistance to wear. Consequently the nanocomposite Cr₃C₂-25NiCr coatings with plasma treated surface can be applied to sliding friction pairs and can operate as protective coatings.

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