Healing effect in coatings deposited by hybrid technology of vacuum electro-spark alloying, pulsed cathodic arc evaporation, and magnetron sputtering using Cr$_3$C$_2$-NiAl electrodes

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Abstract. The single- and multilayer coatings were deposited by methods of vacuum electro-spark alloying (VESA), pulsed cathodic arc evaporation (PCAE), magnetron sputtering (MS) and by hybrid VESA-PCAE, VESA-MS and VESA-PCAE-MS technologies. Cr$_3$C$_2$-NiAl electrodes obtained by self-propagating high-temperature synthesis (SHS) were used for coating deposition. The results of structural studies by scanning electron microscopy are presented. It was shown that the surface defects of the VESA layer can be successfully healed by applying the upper layer by ion-plasma PCAE or MS methods.

1. Introduction
A promising direction in the aerospace, automotive, metallurgical, and oil industries is the using of ceramic coatings based on chromium carbide (Cr$_3$C$_2$) to improve the performance and increase the service life of key components of equipment operating in adverse conditions [1, 2].

Chromium carbide has a high hardness, wear and corrosion resistance and is used as a hard component of ceramic materials [3]. Such materials are usually used to obtain the coatings that are resistant to wear at high temperatures [4]. The most popular material based on chromium carbide is Cr$_3$C$_2$-NiCr [4-7]. The NiCr metal binder reduces the oxidation rate, which ensures high heat resistance of coatings [5]. Therefore, Cr$_3$C$_2$-NiCr coatings are widely used to improve erosion and abrasion resistance, as well as wear resistance at temperatures above 500 °C, but at normal temperatures have low mechanical properties [6, 7]. As shown earlier on example of TiC-NiAl coatings promising binder is NiAl [8]. NiAl in comparison with NiCr has better corrosion resistance in KCl and KCl/K$_2$SO$_4$ at T=600°C. For example, the thickness of the layer of corrosion products and the depth of corrosion in the NiAl coating are 20-70% less than those obtained for NiCr coating [9]. Note that Cr$_3$C$_2$-NiAl coatings have great potential and number of publications devoted to this compound is strongly limited.

Cr$_3$C$_2$-based coatings can be manufactured using various technologies, such as high-velocity flame spraying [10, 11], atmospheric plasma spraying [11], laser thermal spraying [12], or cladding technology [13]. The method of electrospark alloying (ESA) is of interest because the overheating of...
substrates can be excluded during deposition while providing the same adhesion as welding technologies. Note, that electrospark alloying process can be conducted in liquid, air, inert and neutral gas environments, or vacuum (VESA) [14]. Control of the environment allows to improve the quality of coatings. Significant advantages of ESA technology are also its economic efficiency, lack of strict requirements for surface preparation before application, high adhesion, low thermal impact on the substrate [15]. Good adhesion between the coating and the substrate is achieved by mixing the molten substrate material with the deposited material, but the presence of the substrate material can significantly affect the properties of the coatings. ESA coatings have a high surface roughness and defectiveness, which contributes to rapid wear of coatings at high temperatures and exposure to aggressive media. Therefore, combined technologies are used to improve the properties of ESA coatings. The deposition of the top layer for ESA coatings by micro-arc oxidation is known [16]. Laser treatment is also used as a modification of ESA coatings. Different effects including healing of microcracks and pores, increases microhardness by 20 %, corrosion resistance by 30% and reduces the coefficient of friction by more than 20 % were reported [17, 18].

The different vacuum methods of physical vapor deposition can be used to eliminate of disadvantages of ESA. Pulsed cathodic arc evaporation (PCAE) allows to produces the high-quality thin coatings using ceramic cathode without cracking of it [19, 20]. The main disadvantages of the arc evaporation method are the thermal stress activated destruction of ceramic cathodes, and the presence of a droplet phase on the surface of coatings [21]. The use of the pulse mode allows minimizing the thermal effect on the cathode and substrate and high temperature differences, as well as partially or completely eliminating the formation of the droplet phase [22, 23]. To reduce the effect of the droplet phase on the properties of coatings, it is promising to use the method of magnetron sputtering (MS), which allows coating on various substrates with low defect density and dense homogeneous structure with a uniform elemental distribution over the coating thickness [24-26]. ESA-MS technology application increased hardness, impact wear resistance, and corrosion resistance of ESA coatings 1.5-2 times [8]. Modification of ESA coatings by MS can change the physical and chemical properties [27].

This work is devoted to the study of top PCAE, MS, and PCAE-MS layers effect on the surface structure of the ESA coatings when Cr2C2-NiAl electrodes were used for deposition.

2. Materials and Methods

Cr2C2-NiAl electrodes for vacuum electrospark alloying, pulsed cathodic arc evaporation and magnetron sputtering, were synthesized from exothermic powder mixtures using SHS casting technology. The electrodes with sizes of 4 × 4 × 50 mm² (for VESA) and 10 × 10 × 50 mm² (for PCAE) and Ø120 × 10 mm (for MS) were cut from the central parts of the synthesized workpieces using an electroerosion machine. The 40x steel (similar to 5140 steel) discs Ø30 × 5 mm in size were used as the substrates. Before deposition the substrates were subjected to ultrasonic cleaning in isopropyl alcohol for 5 minutes at the installation UZDN-2T. All coatings were produced using a unit based on the UVN-2M pumping system (Russia), which includes of 3 different modules for VESA, PCAE, and MS processes. VESA coatings were obtained using a typical CNC 3D module (figure 1a), adapted to work in vacuum and various gas environments.

VESA deposition was performed at the following processing parameters: residual pressure of 10 Pa, direct polarity (electrode-anode), voltage of 100 V, pulse duration of 20 μs, pulse repetition frequency of 100 Hz, electrode rotation speed below 1000 rev/min, passes number of 20, and treatment area diameter of 20 mm. To carry out the PCAE process, a module equipped with an evaporator of the original design was used (figure 1b). The working gas pressure was 0.4 Pa, the residual pressure 4x10⁻³ Pa. Ar (99.9995%) was used as a working gas. The ignition voltage and frequency were 15 kV and 10 Hz, respectively. The arc discharge voltage ranged from 160 to 200 V. To increase the adhesion preliminary cleaning was performed in the vacuum when negative bias voltage (2 kV) was applied to substrate for 5 min during arc discharge. Direct current MS (figure 1c) were conducted at current of 2 A, voltage of 500 V, distances from the target of 80 mm, and total pressure of 0.2 Pa. Prior to MS deposition the substrates were etched using Ar + ions with an average
energy of approximately 2 keV for 20 minutes using a slot-type ion source (figure 1c). The scanning electron microscope (SEM) Hitachi S-3400N with energy dispersive analysis system NORAN System 7 was used for structural analysis.

![Image 1a](image1.png) ![Image 1b](image2.png) ![Image 1c](image3.png)

*Figure 1. Workspace of vacuum machine with VESA (a), PCAE (b), and MS (c) modules*

### 3. Results and Discussion
Elemental composition of Cr$_3$C$_2$-NiAl produced by VESA, PCAE, and MS methods is given in the Table 1.

| Method | C  | Cr  | Al  | Ni  | Fe  |
|--------|----|-----|-----|-----|-----|
| VESA   | 7.5| 34.4| 1.0 | 9.5 | 47.6|
| PCAE   | 38.3| 49.7| 1.2 | 10.8| -   |
| MS     | 41.6| 43.3| 1.6 | 13.5| -   |

The VESA coating has a high concentration of Fe, equal to 47.6 at. %. The presence of a substrate material (Fe) in the coating is a characteristic feature of the ESA process. Low C content (7.5 at. %) indicates some decarburization of the VESA coating during deposited in vacuum. Note that value of carbon concentration can be measured by EDS with high mistake due to high surface roughness. The contents of Cr, Ni and Al in the coating were 34.4, 9.5 and 1.0 at. % respectively. The concentration of carbon in PCAE sample is 38.3 at. %. This value is 5.1 times higher than that for the VESA sample. Difference may be due to the physical features of the deposition methods. Iron is absent in the PCAE coating. Cr, Ni, and Al concentrations in the PCAE sample increased on 44, 13 and 20 % as compared to VESA coating. When using the MS method, the content of C (41.6 at. %) and Cr (43.3 at. %) became close to stoichiometric, and the concentration of the other elements increased slightly compared to the VESA sample. Note that concentrations of the main coating elements minor changed for PCAE and MS samples.

Figure 2 shows the typical SEM images of surface of VESA coatings.
Figure 2. Top-view SEM images of the VESA coatings

It can be seen that the surface of the VESA coating contains the few types of defects. Cracks, condensed droplets and splashes from the molten electrode material are observed. The cracks evenly distributed over the entire surface of the coating, their width is within 0.35-2.0 microns. The concentration of defects (cracks) is 7.1% of the observed surface area of the coating. A possible cause of cracking may be an extremely rapid temperature fluctuation during the deposition process, resulting in thermal stress [28]. However, we note that locally the coating is smooth, without defects (see insert on figure 2). To reduce the defect concentration, deposition parameters such as frequency, pulse duration, voltage, polarity, electrode rotation speed and number of passes were varied. However, it was not possible to exclude the cracks formation. The solution to this problem is the application of the top layer deposited by PCAE and MS methods.

No cracks and pores were found on the surface of the PCAE coating, and there were no areas of cohesive failure (figure 3).

Figure 3. Top-view SEM images of the PCAE coatings

However, pronounced inclusions of the condensed droplet phase characteristic of coatings deposited by the cathode-arc method [29, 30] are observed on the surface. Spherical droplets ranging in size from 0.2 to 45 microns are evenly distributed and occupy about 13% of the surface area of the coating. The droplet phase sizes are comparable with the previously obtained data for arc deposited coatings [31]. Note that the chemical composition of the droplets corresponds to the composition of the coating, which indicates the melting and evaporation of the cathode material.
MS coating (figure 4) showed a homogeneous surface morphology with a small number of surface defects of fragmentation and droplet forms [32, 33]. Surface defects can be associated with partial melting of the material during sputtering and with local chipping due to high internal stress in the coating [34].

The droplet/shard size ranged from 0.1 to 2 microns. Concentration of defects (< 2% of the surface area) is significantly smaller than for coatings obtained by PCAE.

PCAE coating deposited over VESA layer inherits its topography and defect structure (figure 5).

The area occupied by cracks decreased from 7.1 % for VESA sample down to 1.2 % for VESA-PCAE coating. A reduced amount of droplet phase was observed on the surface. Average size of defects was less than 10 microns. Figure 5 shows that the deposition of the top layer contributes to the healing of cracks.

The VESA–MS coating also inherited the relief of the bottom layer with its characteristic cracks and splashes of molten material (figure 6).
Figure 6. Top-view SEM images of the VESA–MS coatings

The observed shard phase was typical for MS deposited Cr$_3$C$_2$-NiAl coating. Note that surface area occupied by cracks after deposition of the top MS layer onto the VESA sample decreased to 3.5 %. The crack width for VESA-MS coating was 0.2-1.9 microns, and the droplet phase sizes were within 0.2-2 microns.

The results of structural studies for multilayer VESA–PCAE–MS coatings in plan-view mode are shown in figure 7.

Figure 7. Top-view SEM images of the VESA–PCAE–MS coatings

Sample inherits the different defects typical for each deposition method but contains less pronounced crack network. The application of the top layers deposited by PCAE and MS methods helps to heal the cracks of the VESA in this case, the PCAE layer provides high adhesion of the thin layer inside and around the edges of the crack, and magnetron sputtering creates a dense structure on top of it and completely seals the open cracks. This is clearly seen in the cross-section image of the VESA-PCAE-MS coating (figure 8). The thickness of the VESA layer was ~30 µm, the second PCAE layer was 1 µm, and the upper MS layer reached thickness of 3 µm.
The PCAE layer lies on the edges of the crack, and the MS layer finally eliminates the defects of the VESA layer and aligns the surface of the coating. Thus, the observed improvement in the surface quality of VESA coatings when applying the top PCÆ/MS layers will allow the use of hybrid technology to increase the tightness of coatings and improve its corrosion and oxidation resistance.

4. Conclusion
The Cr₂C₂-NiAl coatings were obtained by VESA, PCÆ, MS methods and by combination of mentioned methods. The structural studies showed that surface of VESA coatings contained droplets and splashes of condensed molten material, as well as cracks. Last are the main defects and are critical for practical application. After deposition of the top layers by PCÆ and MS, as well as by PCÆ–MS, the crack width decreased by 80% according to the data obtained in the plan-view SEM observation. Investigation of the VESA-PCÆ–MS sample in the cross-section mode revealed complete filling and isolation of cracks by the upper layers. Thus, surface defects of VESA layer can be successfully healed by applying the top layers by means of PCÆ, MS, and PCÆ–MS deposition.

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Figure 8. Cross-section SEM image and EDS map of the VESA–PCÆ–MS coatings
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