Mass-transfer kinetics, structure, and tribological properties of coatings deposited on steel in Ar or N2+O2 by electro-spark alloying using Cr3C2-NiAl electrodes

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Abstract. Multicomponent coatings were obtained by electro-spark alloying using Cr3C2-NiAl electrodes, in air and in argon medium at direct and opposite polarity. Cr3C2-NiAl electrodes were manufactured by self-propagating high temperature synthesis. Mass transfer kinetics was determined by gravimetric method. The structure and composition of the coatings were evaluated by scanning electron microscopy and energy-dispersive analysis methods. Friction coefficient was measured using pin-on-disk test. Roughness parameters and wear tracks were studied by optical profilometry. It was found that the opposite polarity in combination with a protective environment is optimal in terms of growth rate, structure and tribological properties. The coatings obtained by the best regime had a relatively low roughness (Ra=4 μm), high wear resistance and a low friction coefficient at the level of 0.18.

1. Introduction
To improve the properties and increase the service life of important equipment components exposed to wear, high temperatures and aggressive environments, coatings based on chromium carbide, Cr3C2 [1-3], which has high mechanical characteristics and corrosion resistance, are used. The introduction of a NiCr metal binder into the coating composition reduces the coefficient of friction [4] and increases the resistance to oxidation at high temperatures [5]. Such coatings are also used to reduce abrasive and erosion wear at 850 °C [6]. Increasing the heat resistance to temperatures of 1100 and 1200°C is achieved by using of NiAl binder [7]. The positive role of the NiAl was previously shown by the example of TiC-NiAl coatings [8]. It can be noted that NiAl is superior to NiCr in terms of corrosion resistance in KCl and KCl/K2SO4 at T = 600 °C. [9]. Cr3C2-based coatings are usually manufactured by thermal spraying [10-12]. A promising method to obtain these coatings is electro-spark alloying (ESA). The method has the following advantages: simplicity of equipment, high degree of use of the material, no strict requirements for surface preparation before deposition, high adhesion of the coating, low thermal impact on the substrate, satisfactory surface roughness, easy control of parameters and deposition conditions, composition control due to different media [13-16]. The aim of this work is to study the influence of the gas medium on the mass transfer kinetics and tribological properties of coatings obtained by ESA using the Cr3C2-NiAl electrode.

2. Materials and Methods
Electrodes 4×4×50 mm in size for ESA were cut from a workpiece obtained by self-propagating high-temperature synthesis (SHS) technology by SHS-casting method. The coatings were deposited onto
5140 steel discs Ø30×5 mm in size using the "Alier-Metal 303" machine with the following parameters: current of 120 A, voltage of 20 V, pulse duration of 20 µs, frequency of 640 Hz. Two types of polarity were used: DP - direct (cathode is a substrate) and OP - opposite (cathode is an electrode). The coatings were deposited in air or Ar at a normal pressure for 30 min. The mass transfer kinetics was studied by gravimetric method using analytical weights KERN 770. Morphology, elemental and phase composition of the coatings were estimated by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) on a Hitachi S-3400N microscope with the prefix Noran 7 Thermo. Tribological tests to determine the friction coefficient were carried out on the Tribometer CSM Instruments device according to the “pin-on-disk” scheme. The samples were tested in contact with a 6 mm diameter Al₂O₃ ball at room temperature with a linear velocity of 10 cm/s at a normal load of 1 N. An optical profiler "WYKO NT 110" was used to study the coating’s surface roughness and wear tribo-tracks.

3. Results and Discussion

Mass transfer characteristics, such as a total weight gain of the coating (ΣΔC), total erosion of the electrode (ΣΔE), coating growth rate (Vc), and electrode erosion rate (Ve), are presented in Table 1.

| Mode | Atmosphere | ΣΔC, mg | ΣΔE, mg | Vc, mg/min | Ve, mg/min |
|------|------------|---------|---------|------------|------------|
| OP   | Ar         | 0.34    | 0.45    | 10.3       | 13.6       |
| OP   | Air        | 0.31    | 1.06    | 9.3        | 31.7       |
| DP   | Ar         | 0.39    | 0.62    | 11.7       | 18.6       |
| DP   | Air        | 1.12    | 1.66    | 33.7       | 49.7       |

The obtained data indicate a weak influence of the medium on the growth characteristics of the coating in the opposite polarity mode. The total gain and growth rate of the coating were 0.31-0.34 mg and 9.3-10.3 mg/min, respectively. Carrying out the process in air, however, affected the characteristics of the erosion of the electrode, ΣΔE and Vc, increasing them almost twice, which can be attributed to the fact that the erosion is intensified by the use of active oxygen ions in the spark discharge plasma. The transition to direct polarity in the case of argon medium slightly increased the mass transfer characteristics (Table 1). In the case of deposition in a protective environment in the DP mode, the growth rate of the coating and the erosion rate of the electrode were 11.7 and 18.6 mg/min, correspondingly. During the transition to the air medium, Vc and Ve increased 2.9 and 2.7 times, respectively. Other parameters also increased approximately three times. Apparently, in the air at DP there is a strong oxidation of the growing coating, which is confirmed by the data obtained with the help of EDS.

The curves describing mass transfer at ESD are very different (Figure 1). In all cases, when Ar was used, the coating mass increases smoothly, the electrode mass decreases, and the mass transfer kinetics curves have a character close to linear. During the process in the air in the OP mode from 0 to 9 minutes, an increase in mass was observed, after which, by 18 minutes of treatment, the mass of the sample dropped to the initial value. Further processing showed a decrease in the weight of the substrate, probably as a result of the reaction of oxygen with carbon and the formation of CO₂. The decrease in the substrate mass was accompanied by an increase in the rate of erosion of the electrode, which also indicates decarbonization. Similar processes occur during oxidation of carbon-containing ESA coatings during air annealing [17].

The coatings deposited at OP and DP had the same composition, thus Table 2 presents the elemental composition of samples obtained in the OP mode only. The results are averaged over the area of the EDS analysis.
Figure 1. Results of gravimetric analysis of the weight gain of coatings and erosion of electrodes obtained in Ar and air in the OP (a) and DP (b) regimes

Table 2. Concentrations of elements for coatings obtained at OP, at. %

| Atmosphere | C   | Cr  | Al  | Ni  | Fe  | O   |
|------------|-----|-----|-----|-----|-----|-----|
| Ar         | 33.8| 20.8| 1.9 | 4.9 | 30.8| 7.8 |
| Air        | 27.4| 14.5| 1.2 | 1.5 | 27.4| 28  |

For coatings obtained in Ar and air, the concentration of the substrate element (Fe) is observed at the level of 27.4-30.8 at.%. According to the content of the main elements, a significant difference was found between the samples obtained in Ar and in air. The concentration of C, Cr, Ni and Al in the coating obtained in air was lower by 19, 30, 70 and 37%, respectively. It can be explained by reaction of the coating material with oxygen during deposition, which is confirmed by the high concentration of oxygen of 28 at.%. Figure 2 shows SEM-images of the surface of coatings obtained by OP and DP in different gas media.

The samples have a structure typical for ESA coatings. Coatings have surface defects such as cracks, drops and splashes of molten material (Figure 2 (c, d)). On the surface of the sample obtained in argon at OP, small oxidation zones (FeOx) are formed, corresponding to dark gray areas in micrographs. The total area of such areas does not exceed 5% of the coatings area. Aluminum is present as irregular-shaped Al2O3 grains (black dots on micrographs). When ESA was performed in air in OP mode, the area with high oxygen content increases, and takes more than 50%. In this zone, there is the presence of iron and chromium oxides (dark gray areas). Areas with minimal oxygen content appear in the images as light gray areas. Note that Al2O3 particles are also found on the surface of the sample. Similar results on the influence of media on the structure of coatings were observed for coatings obtained in the DP mode. The roughness of the coatings deposited at OP in Ar and in air was 4.0 and 3.6 µm, respectively. When using DP, the roughness of the coatings obtained in Ar was equal to 3.6 µm, and when doped in air, Ra=4.6 µm. In the case of deposition in argon during the transition from OP to DP, a decrease in roughness is observed, as shown in [18].

The results of tribological tests are shown in Figure 3. The coating deposited in argon at OP had the lowest and most stable friction coefficient (f). The value of 0.22 was achieved at the first contact of the counter-body with the surface of the coating, after which at a distance of 3 to 50 meters the average coefficient of friction was 0.18.
Figure 2. Top-view SEM-images of the coatings: a – OP in Ar, b - OP in N₂+O₂, c - DP in Ar, d - DP in N₂+O₂

Figure 3. Friction coefficient of coatings obtained in Ar (1,3) and air (2,4) at OP (1,2) and DP (3,4) modes. Insert shows the 2D profiles of the wear tracks of samples obtained at DP in Ar (a) or air (b).
Close values were obtained for the coating deposited in the air in the OP mode. The friction coefficient of this sample at the beginning of the test had a value of 0.14, and throughout the distance it gradually increased to f=0.18. In the case of DP and Ar medium, f increased to 0.37 at a run length of 3 m, then the friction coefficient gradually increased and stabilized at 0.67. The coating obtained in the air in the DP mode also showed a jump of f at a distance of 20-50 m, the coefficient of friction gradually increased from 0.3 to 0.4. As shown on insert in Fig. 3 the wear of coatings is within the roughness and is difficult to estimate it.

4. Conclusion

Wear-resistant coatings were obtained by electro-spark alloying using Cr$_3$C$_2$-NiAl electrode. ESA was carried out in different gas media at direct and opposite polarity. According to SEM data, oxygen-containing zones were present on the surface of all samples, which in the case of argon environment were 5 %, and for air were about 50 % of the total surface area. The roughness parameter Ra of the coatings depended on the working medium and was 3.3-3.6 μm for samples obtained in Ar, and 5.4-5.6 μm for coatings manufactured in air. The friction coefficient of the coatings depended more on the polarity than on the gas medium. Samples deposited in the opposite polarity mode had the lowest coefficient of friction in the range of 0.14-0.20.

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