COMPOSITION, STRUCTURE AND TECHNOLOGY FOR PRODUCTION OF ELECTRODE MATERIALS FOR ELECTRIC SPARK RESTORATION AND STRENGTHENING OF WORN-OUT PARTS*

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The electrode materials for producing electric spark coatings of Colmonoy–WC alloy containing 10–70 wt.% WC and hard alloys using TiC, Mo₂C, TiN, Co, Cr, Ni, Al were developed. The phase composition, structure, mass transfer kinetics, hardness and wear resistance of electric spark coatings of the developed alloys were investigated. It was shown that in Colmonoy alloys, Colmonoy–10 % WC and Colmonoy–25 % WC the structure of eutectic character is observed. At pulse energy of 7.5 J the thickness of formed coatings amounted to 3–5 mm. The wear resistance of coatings Colmonoy–WC is 3.5 times higher than that of Colmonoy alloy coatings. It was found that the structure and composition of the developed electrode materials of TiC-based hard alloys allows producing electric spark coatings of up to 100 μm thickness and with hardness of up to 14 GPa. The developed electrode materials were applied under the industrial conditions for strengthening and restoration of worn-out parts of structural steels using electric spark method. 4 Ref., 3 Tables, 7 Figures.

Keywords: electric spark strengthening, electrode materials, restoration of parts, erosive properties, properties of coatings, wear resistance, heat resistance

The producing of thick coatings using electric spark method for restoration of worn-out surfaces has a number of features, which require the development of electrode materials capable of erosion mainly in the liquid phase. The base for these compositions should be metals, erosion products of which adhere well to the base material. The realization of these principles in development of electrode materials will significantly increase the effectiveness of coating deposition on metal surfaces.

The eutectic alloys based on nickel and iron, containing alloying additives of boron, silicon and chromium, are used in producing plasma and detonation coatings [1]. The application of such alloys for electric spark alloying requires investigation of structure and properties of the produced coatings, development of technology for production of compact electrodes and development of technological process.

To produce the wear-resistant (0.5–2.0 mm thick) electric spark coatings the materials of electrodes of alloy with eutectic structure of Ni–Ni₃B system alloyed with silicon and copper and also with WC additives were investigated. The previous investigations [2] proved feasibility of work in this direction. In the present study the investigations were carried out and the technology for producing eutectic Ni–Ni₃B alloy included into Colmonoy class, was developed. The technologies for producing powder mixtures of Colmonoy–WC system with a different ratio of components were developed. The technology was developed and the optimum modes for pressing and subsequent sintering of powder mixtures for production of electrodes were found, where the porosity does not exceed 10 %.

In order to produce coatings of high hardness and thickness of 40–80 μm the most effective direction of modern investigations consists in the development of electrode materials containing refractory compounds with metal bond, optimization of structural composition of this bond and technology for electrodes manufacture. It is feasible to conduct works on creation of electrode materials using TiC, Mo₂C, TiN, Co, Cr, Ni, Al.

Colmonoy–WC system alloys. The electrode materials Colmonoy–WC were manufactured using the following powder metallurgy methods: grinding, mixing, adding of plasticizer, pressing and sintering. For development of electrode material the powder al-

*According to the materials of the work performed within the frames of target integrated program of the NAS of Ukraine «Problems of Life and Safe Operation of Structures, Constructions and Machines» (2013–2015).
loy was used based on nickel belonging to the group of Colmonoy alloys produced using spraying method. This alloy is located in the area of triple eutectic with the main phase of Ni-based solid solution, the melting point of which is approximately 860 °C, that during electric spark allying provides a high mass transfer and the coating thickness sufficient for restoration of worn-out parts. As an additive the copper was used. As a deoxidizer the silicon was used, which is the most effective alloying additive and significantly increases heat resistance. The hardness of the alloy depended on the amount of introduced tungsten carbide.

The tungsten carbide powder was grinded in a ball mill in the medium of rectified alcohol at powder:hard-alloyed balls:alcohol mass ratio of 2:6:1. The time of grinding was 72 h. The size of powder particles of the main fraction was less than 1 μm.

The Colmonoy–WC mixture was produced by grinding–mixing within 4 h at powder:hard-alloyed balls:alcohol mass ratio of 2:8:1. After grinding the mixture was dried in the exhaust hood and mixed with 5 % solution of synthetic rubber in gasoline. The produced mixtures were dried in the exhaust hood and grinded in the sieve 045. The powder mixtures Colmonoy–(10, 20, 25, 30, 40, 50, 70) wt.% WC were produced. The billets of 4×4×70 mm size were pressed in the hydraulic press at pressure of 300 MPa. The porosity of the billets was 40–42 %. The pressed billets were dried in the exhaust hood at 150 °C during 12 h.

The sintering of electrodes was performed in two stages. The preliminary sintering was carried out in the muffle furnace in the hydrogen environment at 800 °C for 2 h. The rate of increasing temperature was 0.06 °C/s. The specimens were placed into the bulky calcined alumina with 2 % additive of graphite grits. The final sintering was performed in the vacuum furnace at 6.67×10⁻³ Pa and 960–980 °C for 2 h. At such a temperature of sintering the specimens have porosity of not more than 10 %, which is optimal. At higher porosity, which is obtained at lower temperature of sintering, the electrode is heated to 800–1000 °C in the process of coating deposition due to decrease in its thermal conductivity, and a significant oxidation of coating material occurs.

Colmonoy alloy has is the structure of hypoeutectic alloy, according to phase equilibrium diagram Ni–Ni₃B. The primary phase is the solid solution of boron, copper and silicon based on nickel with microhardness of 2.3 GPa; the secondary phase is the eutectic consisting of Ni-based solid solution and boron silicide phase based on nickel with microhardness of 7–8 GPa.

The X-ray phase analysis of cast nickel and Colmonoy indicates that during alloying of nickel with silicon and copper the substitutional solid solutions are formed, and alloying with boron results in the formation of interstitial solid solution, as a result of which the lattice parameter of Ni-based solid solution increases from 0.3520 nm for nickel and to 0.3588 nm for Colmonoy (atomic radii are \( a_{\text{Ni}} = 0.124 \), \( a_{\text{Si}} = 0.134 \), \( a_{\text{Co}} = 0.128 \) nm [3]).

The calculation of crystal lattice parameters for WC showed that in this case such elements as boron and silicon are dissolved in tungsten carbide forming substitutional solid solutions. Copper is dissolved in nickel. The microstructure of alloys containing 25, 50, 60, 70 and 80 % WC represents a conglomerate of fine-grained phases of Ni-based solid solution and refractory carbide-boron-silicide combinations. The produced microstructures have typical features of structures of hard alloys WC–Co (mixture of acicul-like phases of WC and metal-based solid solution).

The electric spark treatment of surface of steel 45 was carried out by the developed Colmonoy–WC alloys in ELITRON-52 installation at zero mode with voltage of 100 V and pulse energy of 7.5 J. The mass transfer from anode to cathode was measured by weighing the specimens on analytical balance. The hardness of the coating was measured in PMT-3 device. The value of mass transfer for the electrodes with different contents of WC (from 10 to 70 wt.%) was respectively changed from 2.30 to 0.49 g/cm² with maximum of 2.7 at 25 wt.% WC content.

The carried out investigations of dependence of hardness of the produced coatings on WC content in the electrodes showed a significant increase in hardness from 3 to 8.7 GPa.

For restoration of hardened steel parts those electrodes appeared to be optimal which contain 50–60 % WC. While using the alloy with 50 % WC the hardness of coating was about 5 GPa, however its transfer to the substrate is by 25 % lower than that of Colmonoy alloy. In case of using alloy with 60 % WC the hardness of coating was 7 GPa. Its mass transfer is by 1.5 times lower than for Colmonoy. This is sufficient to produce coatings of up to 2 mm thickness. The alloy with 70 % WC allows producing coatings with hardness of 8.7 GPa, but its transfer is by 5 times lower than that of Colmonoy.

The carried out investigations showed that changing the ratio of components in Colmonoy–WC alloy, according to specific needs, the coatings with different thickness, as well as hardness, can be produced. For example, on steel 45 thickness of electrode Colmonoy material was 4.2–4.8; Colmonoy–25 % WC — 4.0–4.5; Colmonoy–50 % WC — 3.2–3.8 mm. The developed alloys are recommended for restoration of worn-out parts of structural steels.
It should be noted that the surface of coatings produced in installation ELITRON-52 at powerful pulse energy is «hilly» and requires further machining.

The investigation of kinetics of mass transfer of Colmonoy–WC alloy to steel 45 was carried out in installation EFI-46A under the following conditions: oscillation frequency of 100 Hz, short-circuit current of 4 A, operating current of 1.5–2.0 A, energy of one discharge of 0.28 J (which is 27 times lower than the energy in ELITRON-52), period of treatment of 10 min/cm². The kinetics of changes of erosion of the anode and mass increasing of the cathode was determined for each minute of treatment of 1 cm² of the substrate (steel 45).

Figure 1 shows the dependences of mass increment of cathode Δc at electric erosion treatment of surface of steel 45 with alloys of Colmonoy–WC system and standard VK20 alloy.

The microhardness of coatings produced in installation EFI-46A is presented in Figure 2. The comparison of microhardness values of coatings with 10 % WC with the coating containing 70 % WC showed that microhardness of the latter, depending on the distance from the surface, 5 times exceeds the microhardness of the Colmonoy–10 % WC coating.

The investigations of friction and wear of coatings on steel 45 under the conditions of dry sliding friction in air at room temperature according to the shaft–plane scheme were performed in the friction machine at sliding speed of 10 m/s and loading of 10 kg [4]. The coatings at the end surface were treated to smoothness Ra = 0.2 μm. The coefficient of friction f and wear intensity I was determined. For comparison, the specimens of steel 45 without coating were tested. The test results are given in Table 1.

The results of carried out investigations showed that wear resistance of coatings is increased with increase in the content of WC. The wear resistance of coating at application of the electrode with 70 % WC is almost 9 times higher than the wear resistance of steel.

The carried out investigations of properties of electric spark coatings (mass transfer, thickness, hardness and wear resistance) enabled the determination of the optimum content of alloying elements: Cu — 4–5,

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Ic, μm/km</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colmonoy</td>
<td>64.5</td>
<td>0.29</td>
</tr>
<tr>
<td>Colmonoy + 10 % WC</td>
<td>60.8</td>
<td>0.28</td>
</tr>
<tr>
<td>Colmonoy + 25 % WC</td>
<td>58.6</td>
<td>0.30</td>
</tr>
<tr>
<td>Colmonoy + 38 % WC</td>
<td>37.5</td>
<td>0.37</td>
</tr>
<tr>
<td>Colmonoy + 60 % WC</td>
<td>37.0</td>
<td>0.38</td>
</tr>
<tr>
<td>Colmonoy + 70 % WC</td>
<td>18.5</td>
<td>0.30</td>
</tr>
<tr>
<td>Steel 45</td>
<td>160</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Figure 2. Microhardness of coatings versus distance to the surface: 1 — Colmonoy–70 % WC; 2 — Colmonoy–10 % WC

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The developed titanium carbide alloys were used as electrode materials for deposition of protective coatings on the substrate of steel 45. Electric spark treatment of steel surfaces was performed in installation ELITRON-22A at \( I_{op} = 0.8, 1.3, 1.8 \) and 2.3 A. In the process of investigations the mass of eroded anode and mass increment of cathode were determined. The investigations of phase composition of hot-pressed specimens of titanium carbide alloys and structure of protective electric spark coatings of them on the steel substrate were performed in installation DRON-3M in Cu\( K_\alpha \) radiation. The electron microscopic examinations of substructure and fractures of hot-pressed specimens based on titanium carbide as well as formed layers on the steel substrate (in depth) was performed in installation PEMU SelMI. The density of the produced specimens was determined using the method of hydrostatic weighing on analytical balance of the produced specimens was determined using the method of hydrostatic weighing on analytical balance of ADV-200 type, the microhardness was measured in installation PEMU SelMI. The density of the produced specimens was determined using the method of hydrostatic weighing on analytical balance of ADV-200 type, the microhardness was measured in installation PEMU SelMI. The density of the produced specimens was determined using the method of hydrostatic weighing on analytical balance of ADV-200 type, the microhardness was measured in installation PEMU SelMI.

The maximum effect during formation of protective coating on steel substrate is observed when the coating deposited using electrodes of titanium carbide hard alloys, as well as standard alloy TN-20 (TiC–15 % Ni–6 % Mo) and in alloy TiC–Mo\(_2\)C–TiN–Co–Cr it does not exceed 5 \( \mu \)m. In these alloys, according to the data of local X-ray analysis, the grain boundary interlayers, containing Co and Cr, are observed.

In alloy TiC–Co–Ni–C the grains of titanium carbide of 2–10 \( \mu \)m size are separated by the interlayer of the grain-boundary phase of up to 1 \( \mu \)m thickness. The grain-boundary phase according to the data of local X-ray analysis contains cobalt and nickel. In the specimen the pores (mainly at the grain boundaries) of up to 10 \( \mu \)m are observed.

Table 2. Phase composition and microhardness of electrode materials

<table>
<thead>
<tr>
<th>Composition of alloy, wt.%</th>
<th>( H_v ), GPa</th>
<th>Phase composition of alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. TiC–5Mo(_2)C–12Co–5Cr</td>
<td>27.0</td>
<td>TiC(_{1+x}), Cr(_2)C(_3), Mo(_x)C, CoTi(<em>2), TiO(</em>{2a-b})</td>
</tr>
<tr>
<td>2. TiC–5Mo(_2)C–10TiN–12Co–5Cr</td>
<td>25.6</td>
<td>TiCN, Cr(_x)Ti, Co(<em>x)Ti, TiO(</em>{2a-b})</td>
</tr>
<tr>
<td>3. TiC–12Co–3Ni–0.5C</td>
<td>24.5</td>
<td>TiC(<em>{1+x}), ( \beta )-Co, TiO(</em>{2a-b})</td>
</tr>
</tbody>
</table>

Table 3. Phase composition of coatings of alloys based on titanium carbide on steel substrate

<table>
<thead>
<tr>
<th>Composition of alloy, wt.%</th>
<th>Phase composition of coatings on substrate of steel 45</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. TiC–5Mo(_2)C–12Co–5Cr</td>
<td>TiC(_{1+x}), Cr(_2)C(<em>3), TiO(</em>{2a-b}), Co(Ti), Cr(_x)Ti</td>
</tr>
<tr>
<td>2. TiC–5Mo(_2)C–10TiN–12Co–5Cr</td>
<td>TiCN, TiO(_{2a-b}), Co(Ti), Co(_x)Ti, FeTi</td>
</tr>
<tr>
<td>3. TiC–12Co–3Ni–0.5C</td>
<td>TiC(<em>{1+x}), Co(Ti), TiO(</em>{2a-b}), Fe(_x)O(_3), CoO, CoTi(_2)</td>
</tr>
</tbody>
</table>
mogeneity TiC$_{1-x}$ with interplanar distance which is slightly smaller than that in the electrode material. In the coating the solid solution of titanium in cobalt Co(Ti) and titanium oxide TiO$_{2x-1}$ are also present. In addition, the components of the substrate iron and iron oxide Fe$_2$O$_3$ — are manifested in the coating as well as weak lines are observed which may indicate the presence of traces of cobalt oxide CoO and intermetallic CoTi$_2$.

The carried out electron microscopic examinations of surface morphology of the electric spark coatings of alloys based on TiC showed that for all three coatings the presence of two kinds of morphologies on the surface is characteristic: the first one, when the surface is fused, the second one is represented by accumulation of rounded particles of the size from fractions of micron to 10 µm. In the coatings, formed of the first two alloys, the accumulations of fine rounded particles are observed, in case of alloy 3 using the rounded particles are rather uniformly distributed over the surface. In the relatively smooth fused areas the cracks are observed. The investigation of the composition using the method of local X-ray analysis did not show differences in the composition of fused areas and the areas covered with accumulations of particles. The analysis of cross-sections of electric spark coatings of alloys based on titanium carbide on the steel 45 substrate showed that thickness of the formed coatings amounts to 50–100 µm.

On the same specimens the distribution of microhardness in the depth of coatings was studied (Figure 4). From the given data some abnormality in the change of microhardness in the depth of coating, namely, at distance of 10–15 µm from the coating surface the microhardness is 7–9 GPa with its subsequent increase with increase to 12–14 GPa in distance from the surface. The explanation to this phenomenon should be sought in changing the content of elements across the thickness of coatings, for example, of oxygen in the subsurface layer. Thus, the lower the oxygen content, the lower is the presence of solid phases containing oxygen (see Table 3) in the process of formation of electric spark coatings.

The coatings of hard alloys based on titanium carbide were tested under the conditions of friction against the abrasive cloth of silicon carbide of R 1200 gritness. The wear intensity at abrasive friction of coating of alloy TiC–Mo$_2$C–Co–Cr on friction path of up to 15 m is 2 times lower as compared to steel 45.

The wear resistance, determined during friction against the abrasive cloth, is a fundamental characteristic of strength properties of the specimen surface layer. The relative wear resistance in dimensionless units gives a quantitative estimation of resistance to material fracture. The obtained data combined with the data on coating hardness in the cross-section confirm the effectiveness of electric spark strengthening of steel surfaces with the developed materials.

The evaluation of tribological properties of specimens of steel 45 with electric spark coatings deposited in the installation ELITRON-22A at I$_{app}$ 1.3 A using electrodes of the developed alloys based on titanium carbide and those of the standard alloy TN-20 was carried out. The tests for friction and wear were carried out according to the shaft–plane scheme in the friction machine [4] at v$_s$ 0.5, 1.2 and 3 m/s and P = 1 MPa. As the counterbody the ring (shaft) of 40 mm diameter of hardened steel 45 (HRA 42–48) with roughness of working surface Ra = 0.2 µm was used. The tests were carried out in air without lubrication. The friction path amounted to 3 km. The temperature in the contact zone was measured at distance of 0.3 mm from the friction surface. The wear rate was determined by weighing the specimen with coating before and after tests.
Figure 5 shows the dependence of wear intensity of electric spark coatings of the developed electrode materials on steel 45 substrate at different sliding speeds. The temperature in the contact zone changed depending on sliding speed in the range of 92–275 °C. The temperature growth in the contact area in all the pairs with increase in the sliding speed results in increase in wear intensity and reduction in friction coefficient. The investigations showed that the coatings produced at sliding speed of 2 m/s during friction against steel 45 have a high wear resistance and can be used in friction pairs.

Practical application of the developed electrode materials. The application of new composite electrode materials Colmonoy–WC allows producing electric spark coatings of up to 2–4 mm thickness with wear resistance 5–10 times higher than that of steel 45. By changing the ratio of components of Colmonoy and WC it is possible to produce coatings on the structural steels with a wide spectrum of properties. To restore the parts of steel St3 or non-hardened steel 45 it is rational to use coatings of alloy containing up to 25 wt.% WC. To restore the parts of hardened steels it is necessary to use coatings of alloy containing 50 wt.% WC. The work was carried out for the practical application of materials and technology of electric spark strengthening and restoration of metal surfaces at the enterprises «Tekhmashkompani» and «Ukrmetallurgremont» (Dneprodzerzhinsk, Ukraine).

One of the causes of fracture of machine parts is fretting corrosion, which occurs at the interface between the two bodies contacting with each other. The combination of natural corrosion with fretting- and mechanical wear of two surfaces having a relative small mutual displacement results in a significant increase in the degree of wear of surfaces and the danger of local fracture. The wear has a form of so-called pits (cavities), reaching a considerable depth. To such pairs the contacting surfaces of bearing, nicks, key connections, press fits, parts of electric motors, cam mechanisms and adjoining shafts belong. These pits lead to fatigue fracture and local fracture. Removing of these pits, especially on the parts where thermal effect on the metal is not admitted, is almost impossible. Only electroerosion treatment allows correcting this defect, but in this case the depth of pits can not exceed 0.4 mm. Colmonoy–WC alloy developed by the authors allows increasing the spot thickness of the deposited layer to 1.8 mm, which allows considerably expanding the range of repairable parts.

Colmonoy–WC alloy was successfully used at the enterprise «Tekhmashkompani» for restoration of rods of mine hydraulic support posts (Figure 6) operating in wet environment, and at long operation the spot cavities are formed on the surface of rod in the place of contact with the lower and upper supports of the post, leading to a loss of tightness in the assembly and a sharp decrease in the load, perceived by the post. This causes a need in repair of supports. The electroerosive elimination of cavities with subsequent smoothing instead of currently applied surfacing of the whole surface of rod with subsequent machining allowed a significant reducing the restoration period of the support and 3 times shortening the repair costs.

The industrial tests of Colmonoy–WC alloy showed that according to a number of values it is superior to the alloys of VK and Stellite type, which at the present time are applied in electric spark restoration. The maximum thickness of the deposited layer was increased from 0.5 to 1.8 mm.

Under the industrial conditions the technology of electric spark deposition of coatings was implemented for restoration of seat surfaces of axles of crane trolleys of overhead cranes, seat holes in the body of axle of crane trolley, seat holes of bearings in the lids of electric motors and for strengthening of tools. The axle of the crane trolley has diameter of 100 mm and length of 700 mm. It is manufactured of steel 45. In the process of operation the seat surface at the ends of axles of 40 mm width is worn out. The amount of...
wear reaches 0.4 mm. The restoration is performed completely without subsequent machining. The operator determines the required thickness of coating and restoration and, by selecting one of the nine modes of installation EIL8a, deposits the required layer on the surface of the part. The restoration of seat holes of bearings in the lids of electric motors is carried out using the same technology.

Electric spark alloying was used to restore the shafts of electric motors. Previously, these shafts were replaced by the new ones. The restoration of shafts using the method of electric arc surfacing on the worn-out bearing seats of metal alloys showed that as a result of high temperature of surfacing the structural changes occur in steel of the shaft, and, therefore, it provokes a deformation which cannot be corrected using machining. In the electric motor the beat appeared and it became unfit for operation. The problem was solved by using the method of electric spark alloying. Electrode material Colmonoy–50 % WC was used at the enterprise «Elektromash» (Sumy, Ukraine) for local strengthening of plough shares in installations «Elitron-22A» and «Elektron-52A» and restoration of mill rolls and seats of industrial fans (Figure 7).

Conclusions

1. The technology of producing eutectic alloy Ni–Ni$_3$B (Colmonoy) with WC additives was developed. The presence of eutectic structures in the designed electrodes was revealed. It is shown that the hardness increases from 2.8 to 8.7 GPa with increase in WC content, respectively, for Colmonoy and Colmonoy–70 % WC alloys. The thickness of coatings is reduced from maximum of 4.2–4.8 mm for Colmonoy to 3.2–3.8 mm for the alloy with 50 % WC. The microstructure of the produced coatings has a character of thin conglomerate of phases based on nickel and WC. The wear resistance of coatings of Colmonoy–WC is 3–5 times higher than the wear resistance of steel 45.

2. The coatings on metallic substrates deposited with electrodes on TiC base have thickness of 50–100 μm, about 80 % of continuity and microhardness of 12–14 GPa. During sliding friction the wear resistance of coatings of the developed alloys based on TiC is 2–4 times higher as compared to the coatings of standard alloy TN-20.

3. The implementation of technology of electric spark treatment of worn-out surfaces and of new electrode materials 1.5–2 times increases the resistance of parts and tools and 3–5 times shortens the costs associated with the repair of equipment.


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