



SURFACE STRUCTURE MODIFICATION AND HARDENING OF Al-Si ALLOYS

Denis A. Romanov
Stanislav V. Moskovskii
Viktor E. Gromov



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Contents

Introduction	viii
1. Electroerosion resistant composite materials and coatings of electrical contacts	1
1.1. Problem of increasing the electrical erosion resistance of the contacts of the switches of powerful electrical networks	1
1.2. Features of the formation of bulk materials of arc-resistant electrical contacts	2
1.3. Hardening of electrical contacts by spraying electroerosion-resistant coatings	11
1.4. The purpose and objectives of the study	14
2. Equipment, materials and research methods	16
2.1. The rationale for the choice of materials for conducting electric explosion spraying of composite coatings	16
2.2. Electric explosion installation EVU 60/10 M	21
2.3. Vacuum pulsed electron-beam installation SOLO	23
2.4. Processing modes, methods of structure research, phase and elemental composition and properties of electroexplosive coatings	24
3. Electroerosion resistant electric explosive coatings for electromagnetic starters and medium and heavy relays	30
3.1. Structure of electroerosion-resistant coatings of the SnO ₂ -Ag system	30
3.2. Structure of electroerosion-resistant coatings of the CdO – Ag system	42
3.3. Properties of electroerosion-resistant coatings of SnO ₂ -Ag and CdO-Ag systems	57
3.4. Conclusions	62
4. Electroerosion resistant electric explosion coatings for heavy loaded DC and AC contacts	65

4.1.	Structure of electroerosion-resistant coatings of the CuO–Ag system	65
4.2.	Structure of electroerosion-resistant coatings of the ZnO–Ag system	78
4.3.	Properties of electroerosion-resistant coatings of CuO–Ag and ZnO–Ag systems	98
4.4.	Conclusions	107
5.	Structure and properties of electroexplosive wear and electroerosion resistant coatings	110
5.1.	Surface roughness of the surface of pseudoalloys of coatings of the Mo–Cu system	110
5.2.	Features of surface structure and transverse sections of pseudo-alloy coatings of the Mo–Cu system	113
5.3.	Surface roughness of pseudo-alloy of the W–Cu system coatings	124
5.4.	Features of surface structure and transverse sections of pseudo-alloy coatings of the W–Cu system	126
5.5.	Formation of dynamic mesorotations of sprayed coating structures in the electric explosion method	133
5.6.	Features of the surface topography, structure, elemental and phase composition of electric explosive Mo–C–Cu and W–C–Cu systems coatings hardened by synthesized carbides	136
5.7.	Features of the surface topography, structure, elemental and phase composition of electric explosive Ti–B–Cu system coatings hardened with synthesized borides	143
5.8.	Surface topography of electroexplosive coatings of the TiB ₂ –Cu system	146
5.9.	Study of the structure, elemental and phase composition of electroexplosive coatings of TiB ₂ –Cu systems	148
5.10.	Study of surface roughness of electroexplosive coatings of the TiB ₂ –Al system	158
5.11.	Structural–phase states of TiB ₂ –Al system coatings	160
5.12.	Properties of electroexplosive wear and tear and electro-erosion resistant coatings	163
5.13.	Conclusions	167
6.	Structure and properties of electric explosive wear and electroerosion resistant coatings processed by an electron beam	171
6.1.	Surface topography and structural phase states of coatings of Mo–Cu and W–Cu systems of immiscible components	171
6.2.	Surface relief, structure, phase and elemental composition of coatings of Mo–C–Cu and W–C–Cu systems, hardened by synthesized carbide phases of molybdenum or tungsten	178

6.3.	Surface topography, structure, phase and elemental composition of TiB ₂ -Cu system coatings	186
6.4.	The study of surface topography, structure, phase and elemental composition of coatings of W-Ni-Cu and Mo-Ni-Cu systems	190
6.5.	Study of the surface topography, structure, phase and elemental composition of the coatings of the Cr-C-Cu system	201
6.6.	Investigation of the dislocation substructure formed in electroerosion-resistant coatings after electron-beam treatment	205
6.7.	Properties of electroexplosive coatings, electron beam treated	210
6.8.	Conclusions	218
7.	Use of work results	221
7.1.	Use of the results of work in industry	221
7.2.	Use of results in scientific activity and educational process	230
	Conclusions	230
	References	235
	Index	252

Introduction

The reliability of energy systems, minimizing the loss of electrical energy and saving material resources is largely determined by the reliability of electrical contacts. The effective operation of the energy and industrial equipment of the global energy system is due to the reliability of the electrical contacts. The loss of electrical energy and the occurrence of emergency situations occur due to the poor quality of the contacts and their overheating. The main reason for the failure of electrical equipment is the failure of their contact apparatus. This trend is characteristic of most industrial enterprises around the world. To restore the contact apparatus, its electrical contacts are replaced with new ones, or the contact apparatus is completely changed. As a rule, the contacts of the switches of powerful electric networks are a composite material based on a silver matrix with high electrical conductivity and an arc-resistant filler. On the international market, the cost of an ounce of silver is 15.31 USD. More than 50% of the materials spent on the production of electrical contacts remain unused during the operation of the contacts. For the electrical contacts of the switches of powerful electrical networks, only the surface erosion resistance is important. It is economically and technically feasible to develop an approach to the creation of materials when the mechanical strength is ensured by the use of economical substrates, and the special surface properties are ensured by the continuous or local formation of composite coatings on it, whose properties correspond to operational requirements. Material savings with this approach can reach 90%. Modern condensed matter physics as one of its priority areas indicates the development of methods for improving the operational characteristics of various materials is. Given all of the above, hardening of the contact surface of switches of powerful electric networks is an urgent task for the development of modern technologies.

The degree of elaboration of the topic

Scientists all over the world have been actively engaged in the problem of increasing the operational characteristics of electrical contacts operating in conditions of arc and spark erosion for the past 100 years. In 2019–2020, scientists from the USA, China, France, Turkey, Canada, Great Britain, India and other countries have been actively working in this direction. More than a dozen universities in China are working on the creation of electrical erosion materials for electrical contacts. Volumetric materials based on silver, hardened by various MAX phases, have been created by Chinese scientists from the Southeast University under the guidance of Prof. M.M. Liu and scientists from Xi'an University of Technology under the direction of Professor H. Li. Equal channel angular pressing for the production of electrical contact materials is being investigated by a team of scientists led by Professor D. Wang. The work of scientists from the UK under the guidance of Prof. R.A. Veazey is devoted to modelling the structure and properties of arc-resistant electrical contacts. To predict the life of electrical erosion-resistant contacts and manage all factors influencing it, a collaboration of scientists from Thailand (responsible Prof. S. Daocharoenporn) and the USA (responsible Prof. S. Kulkarni) has been created. The electroerosion-resistant coatings obtained to date have insufficient electrical conductivity, which reduces the life of the electrical contacts.



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1

Electroerosion resistant composite materials and coatings of electrical contacts

1.1. Problem of increasing the electrical erosion resistance of the contacts of the switches of powerful electrical networks

In a survey statistical study [1], the main causes of failures and types of malfunctions in 300 cases of electrical component failures are analyzed. As a result of the analysis, it was found that most of the failures of electrical components occurred in the operation of circuit breakers and emergency generators. The main reasons for the failure were the deterioration and failure of electrical components due to a failure in the operation of their contact apparatus. This trend is characteristic of most industrial enterprises around the world.

The phenomenon of electrical erosion is the destruction of the material of the electrodes during electrical breakdown, when an electric arc or spark forms between the electrodes [2, 3]. Electrical erosion is accompanied by the transfer of material between electrical contacts. As a result of the action of numerous discharges, the contacts are gradually destroyed.

At present, compositions based on components with high electrical conductivity and components with high arc resistance are used as materials for arc-resistant contacts of switches of powerful electric networks. As components with high electrical conductivity, silver, gold, copper, etc. are usually used. As a rule, these materials are presented in the form of a matrix in which inclusions of the arc-

resistant component are placed. As components with high arc resistance, tungsten, molybdenum, carbides and metal oxides are used. The combination of the properties of the matrix and the filler allows one to achieve the required level of properties.

Hardening of the surface of the material, and not the entire volume, is economically and technically feasible [4]. It is surface hardening that will save expensive materials of electrical contacts. The development of methods for improving the operational characteristics of various materials is one of the priority areas of modern condensed matter physics. Given the above, the research topic is relevant for the development of new modern technologies.

1.2. Features of the formation of bulk materials of arc-resistant electrical contacts

MAX phases with the formula $Mn + 1AX_n$ (where M is a transition metal; A is an element of group IIIA or IVA; X is C and/or N; $n = 1-3$) are a group of layered ternary compounds with a high modulus of elasticity, as well as good thermal and electrical conductivity, combining the properties of both metals and ceramics [5]. As typical MAX phases, Ti_3AlC_2 [6] and Ti_3SiC_2 [7] efficiently strengthen copper-based electrical contact materials. Professor M.M. Liu et al. [8] fabricated Ag/ Ti_3AlC_2 composites by hot pressing and found that they are potentially suitable for materials of sliding electrical contacts and can be used with high efficiency because they showed good mechanical and electrical properties. In [9], the authors prepared Ag/10 wt.% Ti_3AlC_2 is an electric contact material by powder metallurgy and its resistance to arc erosion was studied, which turned out to be comparable to the commercial Ag/CdO contacts used in contactors. As a rule, the grain size of the matrix phase and the size of the filler are of great importance for the mechanical and electrical properties of the composite.

For example, Professor H. Li et al. [10] reported that finer TiB_2 and SnO_2 reinforcing particles are more beneficial due to less mass loss and relative mass transfer of the silver base of the electrical contact material during electric arc erosion tests. But Professor N. Ray et al. [11, 12] reported that the electrical contact resistance and electrical erosion resistance of the Ag/WC electrical contact material decrease with increasing particle size of the WC. In addition, the structural anisotropy of graphite has been reported to affect the

electrical conductivity and arc erosion resistance of silver–graphite electrical contact materials [13–14]. According to the authors, the influence of the silver grain size and particle size and the preferential alignment of the MAX phases with respect to the properties of Ag/MAX in the electrical contact material was not reported. Powder metallurgy followed by extrusion, drawing, and rolling were used to prepare Ag/C [15], Ag/SnO₂ [16], Ag/CdO [17], Ag/ZnO [17] electrical contact materials. However, these processes change the size of the sample and/or the requirements for high temperature deformation and pressure.

Equal channel angular pressing (ECAP) by the authors of [18–20] was used to prepare materials for the electric contact Ag/Ti₃AlC₂. An Ag/10 wt.% Ti₃AlC₂ composite with a relative density of 99.8% and a homogeneous microstructure was prepared by ECAP at a relatively low temperature of 200°C and a pressure of 37 MPa. Ti₃AlC₂ particles were stratified and predominantly aligned in the Ag matrix after ECAP. The preferential alignment of Ti₃AlC₂ led to the anisotropy of the electrical and compressive properties and the arc erosion resistance of the composite. The properties of the sintered compacted and ECAP sample were investigated. The Vickers hardness of the ECAP sample was about 1.5 times higher than that of the sintered pressed material. The smallest resistivity of 59.3×10^{-9} Ohm · m has an ECAP sample. The maximum compressive and deformation strengths were 805 ± 18.6 MPa and $43.8 \pm 2.2\%$ in the ECAP sample loaded perpendicular to the alignment of Ti₃AlC₂. An ECAP sample with a working surface parallel to the centering of Ti₃AlC₂ showed better resistance to arc erosion. The mechanisms responsible for the anisotropic microstructure and properties were proposed and discussed.

Fine-grained Cu(70–90%)–W composites were successfully obtained [21–23] using nanosized Cu/W powders under vacuum. The sintering process of Cu/W composites is explained by sintering interactions that occur both within the powders and between the powders. Microstructural analysis of Cu/W composites showed that large spherical and nanoscale tungsten particles were uniformly embedded into the copper matrix. The Cu/W interface has a semi-coherent bond and shows good contact. The relative density, hardness, electrical conductivity, and crystal size of W in Cu/W composites increased when the sintering temperature increased from 1000°C to 1090°C. It was found that with increasing copper content, the hardness and grain size of the tungsten grains of the Cu/W composites

decrease, but the relative density and electrical conductivity improve. The ratio of electrical conductivity, sintering temperature, and crystal size W of the Cu/W composites was described using a regression formula.

For the Cu–Ag film contact [24–26], the good boundary properties of the salt allow gliding with a low friction coefficient, a polished worn surface, and high bearing capacity. Under current load conditions, mechanical disconnection and repeated contact of the contacting surface lead to the formation of an electric arc, and damage to the Ag film caused by the electric arc depends on the polarity of the pin and disk. For a positive Cu pin on a disk with a negative Ag film, a rainbow film and transparent LP108 on an Ag film are observed. At the same time, for the negative Cu pin against the disk of the positive Ag film, the removal of the Ag film is observed, and this leads to the suspension of a dark ion–Ag liquid. In both cases, the electric arc does not degrade the LP108. Damage caused by an electric arc and an electric arc on an Ag film can be repaired by ensuring that the contact surface matches exactly.

Three-dimensional continuous composite materials based on an Ag matrix reinforced by a Ni network were obtained by hot pressing of composite Ag–Ni powders with Ni powders deposited on the surface of Ag granules [27–29]. The formation of a three-dimensional continuous Ni network increases the load transferred from the Ag matrix to the second-phase Ni, causing the deformation of Ag and Ni during strain drawing. Joint deformation begins as orientation rotation and refinement; for example, the Ag matrix is shifted by $\{111\}$ $\langle 112 \rangle$, twins by $\{111\}$ $\langle 112 \rangle$ and $\langle 100 \rangle$, which leads to the formation of a texture in the second Ni phase along a certain direction. Finally, continuous three-dimensional nickel networks were torn and pulled into belts parallel to the axial direction of the composite wire. An increase in real deformation can increase the axial length of Ni-grids, thus increasing the hardness and conductivity of Ag–Ni materials for electrical contacts. In addition, the two-dimensional characteristics of electric networks with a high resistance profile increase the hydraulic resistance of molten Ag. Therefore, belt-reinforced Ag–Ni materials for electrical contacts exhibit low mass loss after 100 000 on/off cycles (1.8 mg, only 22.8% of the weight of the sample reinforced with round fibers).

$\text{Al}_2\text{O}_3\text{--Cu}/25\text{W}_5\text{Cr}$ and $\text{Al}_2\text{O}_3\text{--Cu}/35\text{W}_5\text{Cr}$ composites were fabricated by vacuum hot pressing and internal oxidation [30–32]. The electrical conductivity, relative density and Brinell hardness

were measured. The effect of nano- Al_2O_3 and tungsten on the hot deformation of $\text{Al}_2\text{O}_3\text{-Cu}/(\text{W}, \text{Cr})$ composites was investigated using isothermal compression tests using a Gleeble-1500D thermomechanical simulator in the range from 650°C to 950°C and a strain rate of $0.001\text{--}10\text{ s}^{-1}$. The deformed microstructure was characterized and analyzed using optical and transmission electron microscopy. The interaction of the hardening process, dynamic recovery, and dynamic recrystallization was illustrated. It is shown that Cr particles were extruded into strips; W particles underwent a slight deformation during hot compression. In addition, a composite with a higher tungsten content had a higher flow stress. Particles of nano- Al_2O_3 fixed dislocations and inhibited dynamic recovery and dynamic recrystallization. In addition, it is still at the stage of subcrystal formation at 850°C , 0.01 s^{-1} . Therefore, the $\text{Al}_2\text{O}_3\text{-Cu}/35\text{W}_5\text{Cr}$ composite has typical dynamic recovery characteristics. Therefore, the $\text{Al}_2\text{O}_3\text{-Cu}/(\text{W}, \text{Cr})$ composites show good performance at high temperatures.

Tungsten-copper (W-Cu) contact materials are the main components of high-voltage electrical switches. However, the significant effect of arc ablation at high voltage and high current often leads to disconnection and mechanical losses, which seriously affects the safe operation of devices. In [33–35], mechanisms of the destruction of contact materials from tungsten and copper caused by significant arc ablation in the atmosphere of sulphur hexafluoride (SF_6) were studied. The results showed that the arc ablation of contact materials is mainly caused by evaporation and spraying of the copper component, which has a low melting point, followed by ablation and cleavage of the tungsten (W) frame structure. All this increased the surface roughness of the contact materials, and then further accelerated the volatilization of the copper component and the reaction between the contact materials and the SF_6 extinguishing medium. Finally, contact materials have lost their functions of extinguishing the arc and switching current. A simulated experimental work was also carried out, which confirmed the above-described mechanisms of destruction of the contact materials. Due to the instantly high temperature and high voltage occurring during the arc, the Cu and W phases in the W-Cu alloy underwent significant evaporation and mass loss.

Different configurations of the geometry of the two butt electrodes are usually used to study the electrical properties of materials, with the key being how the current flows through the sample. In studies

[36–38], finite element modelling is used to model the response of a direct electric current to an electrically homogeneous sample (based on a SrTiO_3 single crystal) using two butt electrode geometries based on macrocontacts over the entire surface, which is usually used to characterize bulk ceramics or large single crystals and microcontacts, which are used to characterize thin films and local intragranular and intergranular regions in ceramics. Well-known equations for macro- and microcontacts are used to calculate the electrical conductivity of a sample and are compared with eigenvalues to determine their accuracy. The geometric factor indicates the exact values of volumetric conductivity in the presence of a uniform current flow, while the equation of propagation resistance gives the most accurate values of conductivity for a heterogeneous current flow. When microcontacts are used, the reaction is dominated by a small region of high current density near the contact, providing local electrical properties. Interference can occur when areas with a high current density overlap each other, providing a less resistive path for the current to flow, thereby reducing the applicability of the propagation resistance equation. For microcontacts at short distances, the electrical conductivity is overestimated. The accuracy of the propagation resistance equation increases with increasing distance between the contacts and makes an error within 10% when they are separated eight times along the radius of the microcontact. The convergence of the error to values below 10% is becoming increasingly difficult and requires excessively large (and problematic for the experiment) separation distances. For example, to obtain a result with an error below 5%, separation is required that exceeds 28 times the radius of the microcontact. Retention occurs when the size of the sample limits the ability of the current to propagate from the microcontact, thereby increasing the resistance. Since the shape and size of the sample can limit the flow of current, a geometric factor can sometimes be used to determine the exact conductivity. In some cases, interference can balance the limitation to obtain randomly accurate conductivity values.

In studies [39–41], algorithms of computational multibody systems are used to develop detailed models of railway vehicles to predict wear resulting from the dynamic pantograph/contact chain interaction. Wear is predicted using algorithms of computational multi-body systems for various motion scenarios, which include matching the curve with a constant speed and acceleration and deceleration along the tangent to the path. The influence of vehicle vibration in these

various driving scenarios on the contact force is additionally used to study the wear rate of the contact wire. The wear model used in this study takes into account electrical and mechanical stresses. The nonlinear finite element formulation of absolute nodal coordinates, which is suitable for implementation in algorithms of computational multibody systems, is used to model a flexible contact system, thereby eliminating the need to use incremental rotation procedures and joint modeling methods. To obtain effective solutions, both the overhead contact line and the connecting wire are modeled using a cable element of absolute nodal coordinates with insufficient bias. The pantograph elastic contact/contact network composition used in this study allows separation between the pantograph panel head and the contact wire and takes into account the friction effect due to sliding between the pantograph panel head and the contact cable. The approach proposed in the study [39–41] can be used to assess the electrical contact resistance, the contribution of sparking resulting from the separation of the head / contact chain, mechanical and electrical wear, and the influence of the lifting force of the pantograph mechanism on the wear rate. Numerical results are presented and analyzed for studying the wear rates for different scenarios of motion.

The method proposed in articles [42–44] is based on the first principles of the density functional theory for calculating the electronic structure of SnO_2 and rare-earth elements alloyed with SnO_2 . The energy zone and state density of unalloyed SnO_2 and SnO_{2-x} (La, Ce, and Y) were calculated using the Origin Pro 9.0 software for quantitative calculation. Carrying out an experimental test of AgSnO_2 and AgSnO_{2-x} (La, Ce and Y), contact materials prepared by sol-gel and powder metallurgy methods, as well as contact resistance and arc energy, were measured using a simulated electric contact test. In the simulation results, the relative electrical conductivity of SnO_{2-x} (La, Ce, and Y) Y-doped in comparison with pure SnO_2 is greatest. In the experimental results, the minimum and maximum values and the range of variation of the arc energy and contact resistance after AgSnO_{2-x} (La, Ce, and Y) are reduced. The effect of Y-alloyed AgSnO_2 is more obvious and has the highest density. The final simulation and experiment results are in good agreement. Y-alloyed with AgSnO_2 has the best electrical characteristics, followed by La alloyed AgSnO_2 .

Studies [45–47] focus on the wear, friction, and electrical characteristics of the newly developed disk contact design for

sliding electrical contacts. Various types of graphite and copper as combinations of materials, various operating parameters of the contact and, in particular, different directions of the electric current, that is, the polarity of the disk, were investigated in real contact conditions on a special tribological test setup. Electrographite and polymer-bound graphite worked in the coupled contact, against copper and against each other. A pair of polymer-bound graphite / polymer-bound graphite showed the best results for almost all the parameters studied, while a mixed, heterogeneous combination of polymer-bound graphite/electrographite had the worst performance. In addition, all couples containing electrographic material showed unstable contact behavior and generally gave the worst overall performance. The wear of self-conjugate graphite pairs was less than the wear of graphite/ copper couples. The effect of polarity on graphite/graphite material combinations was negligible, while in graphite/copper combinations it was found that the direction of electric current significantly affects disk wear. The wear of a positive graphite disk was 30% lower than that of a negative graphite disk, while the wear of a positive copper disk was 8 times greater than the wear of a negative copper disk. Differences in the boundary contact film were observed in graphite / copper contacts depending on the polarity of the surface, which means that sliding contacts with the current flowing from the graphite disk to the copper disk showed less wear than contacts where the current flows from the copper disk to the graphite disk .

Copper-based materials are widespread industrial products that are widely used in the fields of powder metallurgy, electrical contacts, heat exchangers, etc. However, the ease of surface oxidation limits the durability and efficiency of copper-based components. The authors of [48–50] developed a powder metallurgy process for the manufacture of graphene/copper composites using copper powders, which were first deposited on graphene layers by thermal chemical vapour deposition (CVD). Graphene/copper composites enclosed in a bonded graphene network could then be obtained by vacuum hot pressing. After thermal oxidation (up to 220°C) in humid air for several hours, the authors [48–50] found that the degree of surface oxidation of the samples was much lower than that of their pure Cu analog, and the samples [48–50] showed a smaller increase contact resistance of the interface when used as materials of electrical contacts. As a result, graphene/copper composites showed a significant improvement in oxidation resistance (about 5.6 times)

compared to their pure copper counterpart, thus offering potential applications as new materials for electrical contacts.

Multilayer Cu/Ni-P/Au systems are used as electrical contacts [51–53]. The upper layer of Au is thin and porous. These pores deliver a corrosive medium to the lower layer, which causes corrosion using a galvanic coupling mechanism. Therefore, filling these pores is necessary to increase the life of electronic devices. The pores can be sealed by electrodeposition of poly (methyl methacrylate), which reduces the porosity index (about 97%) and increases the corrosion resistance (about 10 times) of electrical contacts after 10 cycles of electropolymerization. However, an inhomogeneous polymer film was formed during a larger number of polymerization cycles (> 50), which reduced the corrosion resistance.

In papers [54–56], an attempt was made to evaluate the operability of arc contacts as a vital component of the interruption chamber in SF₆ high-voltage circuit breakers with a tension filter. The relationship between the eroded mass caused by interruption of the short-circuit current and various thermal voltage indicators, such as transferred electric charge, square of the current strength and arc energy, were investigated by conducting many experiments with different current amplitudes and arc lifetime. It is shown that none of the known indicators can determine only mass erosion caused by interruption of current. Therefore, to evaluate mass erosion, equations have been proposed that include two of certain parameters. The method using arc energy and the transferred electric charge has the highest accuracy in estimating mass loss [54–56]. However, given the complexity of measuring arc voltage, you can also use another method that uses current and arc lifetime. In addition, the development of erosion during the life cycle of arc contacts is studied. It is shown that the roots of the arc tend to form on new non-eroded sections of the contacts during current interruption, which leads to different erosion rates between the first several and subsequent interruptions due to changes in the contact morphology after the first several switching operations.

The susceptibility of the pin socket to vibration loads is one of the achievements of electrical engineering. Electrical engineering alone is not enough to solve this complex problem. Multiphysics analysis is expected to be the solution to analyze this electromechanical pin-socket dynamic structure. Studies [57–59] develop dynamic contact multiphysical analysis with the formalism of tensor network analysis. The multiphysical model combines the relative speed and position

of the pin in combination with instantaneous contact resistance implemented in an RC network. An innovative method has been developed that allows one to determine the signature of vibrational voltage by the signal-to-noise amplitude. The relevance of the model of multiphysical tensor analysis of networks is illustrated by the example of a 10 mm long socket with uniaxial vibrational voltage of an arbitrary waveform with a passband of 20 kHz. It has been shown that contact resistance can fluctuate more than a thousand times. The vibration-stress state of the pin-socket depending on the parameters of the RC network is also discussed. The proposed multiphysical analysis can be potentially applied to the study of electromagnetic compatibility and signal integrity of assembled electronic equipment and printed circuit boards under conditions of vibrational stresses.

With the rapid development of ultra-high voltage technology (over 500 kV), it is becoming increasingly difficult to meet the high demands of traditional electrical contact materials for ultra-high voltage switches. Copper/graphene composite coatings on a pure copper substrate were successfully fabricated using the simple cathodic electric codeposition method [60–62]. The morphology, structure, coating composition, and porosity of composite copper / graphene coatings were studied. The Vickers hardness of the copper / graphene composite coating increases by about 25% compared to pure copper coating. Adding graphene to a composite coating with a low coefficient of friction of approximately 0.2 increases wear resistance. The thermal conductivity of the copper / graphene composite coating prepared in a galvanic solution with a graphene content of 10 g / l reaches 285.2 W / (m · K) at room temperature, which is 61.9% more compared to a pure copper coating. The average interrupt current of 3.6 A of the copper / graphene composite coating is superior to that of the Cu20W80 alloy, indicating improved resistance to arc ablation. The copper / graphene composite coating provides new opportunities for replacing traditional materials for electrical contacts of ultra-high voltage circuit breakers.

To study the electrical characteristics of AgTiB₂ contact materials with various Ni additives, arc erosion tests were performed 20 000 times at a voltage of 24 V and a direct current of 16 A [63–65]. The morphology and chemical composition of the arc eroded contact surface was characterized by scanning electron microscopy and energy dispersive X-ray spectrometry, the mass change after testing for arc erosion was determined, and the arc energy and arc duration on the working and bursting arc were determined. The mechanisms

of arc erosion are analyzed and discussed. The results show that the mode of arc erosion varies from anodic erosion to cathodic erosion with the addition of Ni. The contact material Ag-4 wt.% TiB₂ with the addition of 2 wt.% Ni has optimal characteristics along with the smallest weight loss, while especially high arc energy and total mass loss are formed at 4 wt.% and 8 wt.% Ni. In addition, the mechanism of arc erosion was discussed based on contact characteristics, thermal properties, and ionization energy of materials. It is believed that excessive addition of Ni is not beneficial for improving arc erosion resistance, since Ni has a great potential for ionization and the possibility of evaporation due to its small difference in the change in enthalpy compared to ionization energy.

The materials of the electrical contact Al₂O₃-Cu/(25)W(5)Cr and Al₂O₃-Cu/(35)W(5)Cr were prepared by vacuum sintering by hot pressing and internal oxidation [66–68]. Relative density, electrical conductivity, and Brinell hardness were measured. The microstructure was analyzed using scanning electron microscopy and transmission electron microscopy. The JF04C electrical contact tester was used to study the electrical contact characteristics of composites. The morphology of arc erosion was analyzed using scanning electron microscopy and a three-dimensional profilometer. Material transfer, as well as the characteristics of the electrical contact, were studied during the operations of closing and opening contacts at 30 V DC from 10 to 30 A. Nano-Al₂O₃ particles fixed the dislocations. The material was transferred from the cathode to the anode. During the melting, evaporation, and atomization of copper during sparking, W particles collect and form needle-shaped skeletons. At the end of experiments [66–68], liquid droplets, needle-like structures, craters and bulges formed on the surfaces of electrodes after arc erosion. In addition, their content and morphology are affected by the tungsten content. When the tungsten content of the dispersed copper matrix increases from 25 to 35 wt.%, The welding power decreases during stable operations. In addition, when the arc duration exceeds 8.86 ms, the Al₂O₃-Cu/(35)W(5)Cr contact material has a shorter average arc duration than Al₂O₃-Cu/(25)W(5)Cr at the same energy arcs.

1.3. Hardening of electrical contacts by spraying electroerosion-resistant coatings

To ensure high electrical erosion resistance and electrical conductivity, at least two components are required, one of which

has high electrical conductivity, and the other has electrical erosion resistance. Obtaining such composite coatings is a complex task, since it is necessary to ensure acceptable adhesion of the coating to the substrate and cohesion of the particles of the composite coating. At the Plasma Focus installation, electroerosion-resistant coatings of the W–Cu system were obtained [69–71]. Tungsten penetrates into the copper substrate to a depth of not more than 25 microns, while its concentration does not exceed 10 at. % However, for contacts of switches of powerful electric networks, pseudo-alloy materials based on the W–Cu system with a higher concentration of tungsten are required.

Condensed from the vapour phase composite materials obtained by high-speed electron beam evaporation and subsequent condensation have a layered structure [72, 73]. The thickness of a single layer is from units to hundreds of micrometers and is set by the operating parameters of the installation. At present, materials based on electroerosion-resistant systems W–Cu, Mo–Cu and Cr–Cu, C–Cu have been obtained [74, 75]. These condensed materials have a lamellar structure with a hierarchy of macro-, micro- and submicron levels. In condensed materials based on copper and chromium, solid solutions of supersaturated chromium are formed and decomposed. the influence of temperature and volume fraction of refractory particles on the kinetics of their growth during liquid-phase sintering of Cr–Cu composites in the temperature range 1150–1350 °C in vacuum $(2-4) \cdot 10^{-3}$ Pa is considered. It was found that the kinetics of growth of medium-sized particles is described by an almost cubic law, and the decrease in their number is determined by an almost inverse relationship: the apparent activation energy ($Q = 113 \pm 10$ kJ/mol) has an order comparable to diffusion in liquid metals. According to the Lifshitz–Slezov–Wagner theory, diffusion coalescence indicates the growth of particles controlled by diffusion. The experimental growth constants are an order of magnitude higher than those calculated in the framework of the classical Lifshitz–Slezov–Wagner theory. An increase in the growth rate constant with a volume fraction of refractory particles varying from 0.4 to 0.7, and a change in the particle size distribution function after sintering for 90 min at 1200°C are consistent with the Ardell model, which modifies the Lifshitz–Slezov–Wagner theory taking into account the effect, the volume fraction of particles according to the kinetics of their growth. The coatings obtained in this way have low adhesion and for this reason are not suitable for practical use. The article

[76] presents and discusses the actual state and prospects of using powerful electron beam technology for the manufacture of metal as well as non-metallic composite materials, mainly for electrical contacts and electrodes.

A technology has been developed for producing condensed gradient composite materials of the Cu–W system using high-speed electron beam evaporation–condensation [77]. Changes in the structure, electrical conductivity, hardness, mechanical properties, tensile fracture of a condensed Cu–W material at ambient temperature and elevated temperatures depending on the tungsten content and heat treatment are studied. New morphological features of the condensed composite material have been discovered that cause a change in the properties of the material. The relationships and correlation dependencies between the tungsten content, structure, strength and hardness of the composite are established.

Production technology, structure, electrical conductivity, friction coefficient, hardness, strength and ductility in the temperature range of 290–870 K of copper–carbon composites with layered structures and carbon content from 1.2 to 7.5 mass. % of sliding electrical contacts of current collectors obtained by electron beam evaporation and vacuum condensation were studied by the authors [78]. A thermodynamic activation analysis of the hardness and strength of the composites was carried out. Correlations between hardness and strength of composites are established.

Scientists at the Siberian State Industrial University are studying the structure and properties of electroerosion-resistant coatings of various systems obtained by the electric explosion method. Thanks to the modernized installation [79] over the past 10 years, it has been possible to obtain coatings with unique properties. These include composite coatings of immiscible components of the W–Cu and Mo–Cu systems with a layered or dispersion-strengthened structure [80–82]. The addition of carbon to the W–Cu and Mo–Cu systems makes it possible to increase the hardness of coatings due to the formation of molybdenum and tungsten carbides [83, 84]. An increase in the hardness of electroerosion-resistant coatings can be achieved by synthesizing titanium borides in a copper matrix [85, 86] or using ready-made titanium diboride powder [87].

Prediction of the properties of formed coatings was based on various physical and mathematical models [88–92]. These models are based on the occurrence of various instabilities during the EES process, such as Rayleigh–Taylor, Marangoni, Richtmeyer–Meshkov,

Kelvin–Helmholtz, etc. In the structure of electroexplosive coatings of all the systems under study, rounded regions with a diameter of 10–30 μm , having well distinguishable thin (from 1 to 2–3 μm) border with the surrounding coating material. The distances between the regions of dynamic rotations, although they do not have a constant value, can be estimated on average as $\sim 10\text{--}50$ μm . The appearance of such formations during EES can be explained as a first approximation from the position of ‘dynamic rotations’ developed by the school of Academician V.E. Panin. The surface structure is stable due to the formation of a system of confined localization sites of embedded atoms. In the places of localization during solidification, deformation of the crystal lattice occurs. Apparently, these are manifestations of the rotational mode of formation of distortions of the structure after its occurrence and solidification. The closeness of the considered distortions and their typicality in the observation field are the properties that form the strength of the developed coatings. It should also be borne in mind that EES is a complex, fast-flowing process associated with the formation of a liquid phase on a substrate. In the works of V.D. Sarychev, A.A. Buneev and other researchers it was shown that vortices are formed near the molten metal due to the development of thermocapillary instability. Thermocapillary instability – an increase in the amplitude of oscillations of the liquid surface in a nonuniformly heated liquid due to the Marangoni effect. In addition to the above, other forces act in the molten metal; for example Marangoni, who showed that fluid would flow from areas with a lower surface tension to higher. The surface tension depends on temperature and this imposes additional force on the movement. A generalization of theoretical ideas about EES and experimental studies was carried out in [93–96].

It is possible to improve the properties of electroexplosive coatings using EBT [97–101]. As a result of exposure to EBT, electroexplosive coatings are nanostructured, their volume is homogenized. The influence of EBT on the structure and properties of electroerosion-resistant coatings was generalized in [102–104].

1.4 The purpose and objectives of the study

A literature review allows us to state that a variety of methods for the formation of bulk electroerosion-resistant composite materials and coatings have various characteristic features. A large number of bulk electroerosion-resistant composite materials was obtained,

however, the formation of similar coatings is associated with a number of unsolved technological problems. In this regard, the aim of this work was to identify the laws and physical nature of the formation of the structure and properties of electroerosion-resistant electroexplosive coatings during the spraying process and subsequent electron-beam processing. To achieve the goal, the following tasks were set and solved:

1) to develop methods for electric explosive spraying of electroerosion-resistant coatings of various systems;

2) to develop methods for electroexplosive spraying of wear- and electroerosion-resistant coatings of various systems with subsequent electron-beam processing;

3) to establish the influence of the parameters of electric explosive spraying and subsequent electron-beam processing on the surface topography, the structure of the coatings in depth and the features of their structural-phase states;

4) to determine the wear and erosion resistance, nanohardness of sprayed coatings;

5) to determine the erosion resistance and tribological properties of the coatings after electron-beam processing in modes that provide a complex of high functional properties;

6) to test the operational properties of sprayed coatings at industrial enterprises.

2

Equipment, materials and research methods

2. The rationale for the choice of materials for conducting electric explosion spraying of composite coatings

It is known that, for example, silver-based composite materials hardened by cadmium, zinc, copper, and tin monoxides are highly resistant to electrical discharge erosion. Therefore, it is of interest from both a practical and scientific point of view the formation of composite electrical coatings of the CdOAg, SnO₂-Ag, CuO-Ag, and ZnO-Ag systems in order to protect copper arc-resistant electrical contacts [105]. The type of coating was selected on the basis of previously obtained conclusions on the production and industrial use of bulk materials.

The choice of M00 brand copper for the substrate material on which coatings for electrical purposes was applied is due to the fact that it includes a set of properties that determine a large area of its application in the electrical industry. These are such properties: high heat sink rate into the volume of the material, high electrical conductivity, corrosion resistance in various environments, good mechanical properties at various temperatures. Copper is used for the production of wires, electrical cables, windings of electric machines, various transformers, copper strips, tires, tapes, collector plates, machine components and parts, electrical contacts of various assortments, etc. [105].