ADVANCED MATERIALS AND TECHNOLOGIES

Structure and Properties of Electroerosion-Resistant Ag–Co–N Coatings Fabricated by a Combined Method

D. A. Romanov^{a, *}, V. V. Pochetukha^a, V. E. Gromov^a, K. V. Sosnin^a, and Yu. F. Ivanov^b

^a Siberian State Industrial University, Novokuznetsk, 654007 Russia

^b Institute of High-Current Electronics, Siberian Branch, Russian Academy of Sciences, Tomsk, 634055 Russia *e-mail: romanov da@physics.sibsiu.ru

Received October 9, 2021; revised October 9, 2021; accepted October 18, 2021

Abstract—Copper-based Ag—Co—N coatings are fabricated by a combined method, which includes electro-explosive spraying, electron-beam treatment, and nitriding. The nanohardness, the wear resistance under dry sliding friction conditions, the coefficient of friction, the electrical conductivity, and the electroerosion resistance of the coatings are investigated, and their structure and phase composition are analyzed.

Keywords: electrical contact, coating, silver, cobalt, cobalt nitride, electroexplosive spraying, nitriding, electron-beam treatment

DOI: 10.1134/S0036029522100196

INTRODUCTION

The reliability of power equipment depend on many factors, including the switching wear resistance of contactors determined by the mechanical and electrical properties of their contacts. Electroerosionresistant contacts are based on a composition of a refractory component and a component with a high electrical conductivity, which is often made of silver. The electrical contacts of the W–Ag [1], Mo–Ag [2], Ag-C [3], Ag-Ni [4], Ag-Cd [5] and Ag-Co [6] systems have found the widest practical application. To ensure long-term and stable operation of electrical contacts, fibers [7], filamentary crystals [8], and spatial networks [9] are sometimes introduced into a silver matrix. Basically, the composite materials used for electrical contacts are produced by powder metallurgy methods [10]. However, the porosity of such contacts can reach 3%, which negatively affects the electrical conductivity.

An alternative to current-conducting composite materials can be materials with a deposited conducting coating (see, e.g., [11, 12]). Electroexplosive spraying of coatings is considered to be promising [13]. Note that this method is also applicable for restoring the surface of electrical contacts during wear, which is useful from the standpoint of economics and ecology.

In [14], we showed that electroexplosive spraying is effective for producing nanostructured electroerosion-resistant coatings on copper contacts. Subsequent electron-beam treatment and nitriding further enhance the properties of such coatings [15]. The aim of this work is to study the structure and properties of Ag-Co-N coatings fabricated by a combined method.

EXPERIMENTAL

The Ag–Co–N coating was formed on a $25 \times 25 \times$ 3-mm M00 copper plate by electroexplosive spraying followed by pulsed electron-beam irradiation and nitriding in a low-pressure gas discharge plasma. The electroexplosive formation of a coating was carried out using an EVU 60/10M installation with the following parameters: the time of plasma action on the sample surface was 100 μ s, the absorbed power density on the jet axis was 5.5 GW/m^2 , the pressure in the shockcompressed layer near the irradiated surface was 12.5 MPa, the residual gas pressure in the working chamber was 100 Pa, and the plasma temperature at the nozzle exit section was 10⁴ K. Two foils made of silver weighing 350 mg and made of cobalt weighing 50 mg were used as a material for spraying. The foils were superimposed on each other and subjected to an electrical explosion at the same time. Irradiation with a pulsed electron beam (20 and 40 J/cm², 200 μ s, 3 pulses) and nitriding (923 K, 3 h) were performed on a COMPLEKS installation.

The defect substructure and the elemental composition were analyzed by scanning (Carl Zeiss EVO50 515 microscope) and transmission diffraction (JEM 2100F microscope) electron microscopy. The phase composition and structural parameters of the samples were studied using an XRD-6000 diffractometer and CuK α radiation. Phase composition was analyzed using the



Fig. 1. Contact resistance R vs. the number of on/off cycles N during electroerosion resistance tests of Ag–Co–N coatings.

PDF 4+ database and the POWDER CELL 2.4 fullprofile analysis software package.

The hardness of the coating was determined with a Shimadzu DUH-211 ultramicro hardness tester at a load of 30 mN on a transverse polished section at a distance of 20 μ m from the surface.

The tribological properties of the coating were studied using a Pin on Disc and Oscillating TRIBO-tester (TRIBOtechnic, France) tribometer. Wear resistance tests were carried out according to the ball–disc scheme at the following parameters: the ball 6 mm in diameter (counterbody) was made of ShKh15 steel, the load was 3 N, the distance was 300 m, the wear track radius was 2 mm, and a ball speed was 25 mm/s. The wear resistance of the coating was determined using the sample weight loss after a test. Samples were weighed before and after tests on a CAUW 220D analytical balance.

Copper contacts with a sprayed coating were subjected to electroerosion resistance tests as part of CJ20 electromagnetic starters in order to determine the number of switching (on/off) cycles. For testing, the AC-3 regime was used for operation in a three-phase alternating current circuit with an inductive load and, the rated voltage was 400/230 V, the frequency was 50 Hz for currents up to 320 A and $\cos \varphi = 0.35$, the number of switching cycles was 7000.

The electrical conductivity was measured on the same stand where electroerosion resistance tests were carried out.

RESULTS AND DISCUSSION

As a result of electroerosion resistance tests, we found that the contacts coated with an Ag–Co–N or WN–WC–W₂C_{0.84}–Ag coating [15] withstand 7000 switching cycles (Fig. 1). The electrical resistance of the contacts with an Ag–Co–N coating do not exceed 10 μ Ω up to 4000 switching cycles, and that of the coatings with a WN–WC–W₂C_{0.84}–Ag coating reaches 15 μ Ω [15]. After 4000 switching cycles, the electrical resistance of the coatings of both systems is 15 μ Ω and decreases by the end of tests. The electrical conductivity of the formed coating is close to the electrical conductivity of silver and is 62.0 MS/m [16].

As in [15], we determined the dependences of the contact voltage and current when one phase was closed, when one phase was lost at zero current, and when one phase was lost at the maximum current. As an example, Fig. 2 shows the dependences of the contact voltage and current on the test time when one phase is lost and the current is zero. The opening time of the contacts in this case is approximately 8 ms. When one phase is closed or when one phase is lost at the maximum current, the opening time of the contacts is 20-25 ms, which is comparable to the results obtained in [16]. Thus, the formed coating fully meets the requirement of rapid arc quenching on opening electrical contacts.

In tribological tests, it was found that the wear resistance of the coated copper sample exceeds the wear resistance of copper by 1.6 times at a comparable coefficient of friction: $\mu = 0.531$ and 0.526, respectively. The low coefficient of friction expands the prospect of using the coatings, for example, for sliding electrical contacts.

The hardness of the coating changes over a very wide range, from 580 to 2500 MPa at an average value of 1400 MPa (the hardness of uncoated copper is 1270 MPa), which is below the hardness of WN–WC–W₂C_{0.84}–Ag coatings (3910 MPa) [15].

The obtained properties of the coatings are caused by their structure and phase composition. The coating thickness was found to be not the same: it changed from 40 to 50 μ m (Fig. 3). The coating is structurally heterogeneous: it contains inclusions of various shapes and sizes. The main element of the coating is silver, and cobalt and copper are present in a much smaller amount (Fig. 4). The detected elements are nonuniformly distributed in the coating. Islands 1–15 μ m in size enriched with cobalt were also detected (Fig. 5).

X-ray diffraction (XRD) studies revealed the presence of solid solutions based on copper, cobalt, and silver and cobalt nitrides in the coating (Fig. 6). The main phases are based on copper and silver and cobalt nitrides are present in small amounts, up to 9 vol %. The fragment of the coating shown in Fig. 7a is formed by regions enriched in silver (c) and cobalt (d) atoms.



Fig. 2. (solid line) Contact stress and (dotted line) current vs. the test time when one phase is lost at zero current (b). Enlarged image of the section indicted by the arrow in (a); \Leftrightarrow indicates loss of phase.



Fig. 3. Structure of the copper base with an Ag–Co–N coating (transverse polished section, SEM): (a) general view and (b) structure of the coating.



Fig. 4. Element distribution over the thickness of the coated sample; zero corresponds to the surface layer of the Ag–Co–N coating.



Fig. 5. Cobalt islands in the Ag–Co–N coating.



Fig. 6. X-ray diffraction pattern of the Ag–Co–N coating.

The coating has a submicro- and nanocrystalline structure formed by crystallites 40-150 nm in size (Fig. 8). Particles 3-5 nm in size are located along the boundaries and in the volume of crystallites.

The results of XRD analysis of the coating area, an electron microscopic image of which is shown in Fig. 8, are presented in Fig. 9. Indexing of the electron

diffraction pattern (Fig. 9b) taken from the coating area selected by a field diaphragm (Fig. 9a) indicates that the coating is multiphase. The presence of the following phases was revealed by dark-field analysis: CoN (Fig. 9c), Ag (Fig. 9d), Cu (Fig. 9e), and CuN_{3.2} (Fig. 9f). Phases Ag, Cu, and CoN form the grain– subgrain structure of the coating. The CuN_{3.2} phase in



Fig. 7. Structure of the coating: (a) bright-field image and images taken with the characteristic X-ray radiation of (b) copper, (c) silver, and (d) cobalt.



Fig. 8. Structure of the Ag–Co–N coating formed on a copper substrate by the combined method.



Fig. 9. Structure of the Ag–Co–N coating formed on a copper substrate by the combined method: (a) bright-field image; (b) electron diffraction pattern taken from the foil region indicated in (a); and (c–f) dark-field images taken with the reflections [111] CoN, [200] Ag, [111] Cu, and [150] CuN_{3.2}, respectively. (b) Reflections used to take dark-field images: (1) (c), (2) (d), (3) (f), and (4) (e).

RUSSIAN METALLURGY (METALLY) Vol. 2022 No. 10

the form of nanoparticles is located along the boundaries of copper and silver grains and in the volume of copper grains.

CONCLUSIONS

Commercially suitable (in structure and properties) electroerosion-resistant coatings for electrical contacts were fabricated. The uniformity of the thickness, hardness, and phase composition of the coatings can be further improved by changing the design features of the electroexplosive spraying chamber.

ACKNOWLEDGMENTS

The investigations were carried out using the equipment of the Structure, Mechanical and Physical Properties of Materials core facility of Novosibirsk State Technical University.

FUNDING

This work was supported by the Russian Foundation for Basic Research (project no. 20-08-00044) and a grant from the President of the Russian Federation for state support of young Russian scientists—doctors of sciences (MD-3954.2022.4) and candidates of sciences (MK-5585.2021.4, MK-4292.2022.4).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- 1. V. K. V. Manikantad and D. Kondayya, "Synthesis of W–AG nanoalloys and computer aided thermal analysis of W–AG nanoalloys based heat sink," Int. J. Recent Technol. Eng. 8, 8822–8825 (2019).
- 2. B. Gao, L. Zhou, C. Zhang, J. Zhu, L. Fu, W. Yang, and D. Li, "Effect of microstructural evolution on mechanical and electrical properties of Ag–Mo thin films," Surf. Eng. **37**, 1143–1154 (2021).
- 3. S. Arai, T. Kikuhara, M. Shimizu, and M. Horita, "Superior electrical contact characteristics of Ag/CNT composite films formed in a cyanide-free plating bath and tested against corrosion by H_2S gas," Mater. Lett. **11**, 1067 (2021).
- H. Li, X. Wang, Y. Fei, H. Zhang, J. Liu, Z. Li, and Y. Qiu, "Effect of electric load characteristics on the arc erosion behavior of Ag–8 wt % Ni electrical contact material prepared by spark plasma sintering," Sens. Actuators, A: Physical 326, 112718 (2021).
- J. Wang, J. Yang, Y. Zhu, G. Zhang, D. Hu, and G. Huang, "Effect of Ni, N Co-doped on properties of AgSnO₂ contact materials," Crystals 11 (6), 707 (2021).
- B. Cagan, M. Erdogan, I. Karakaya, C. Yilmaz, and B. Yurdakul, "Investigation of Au–Ag–Cu alloy elec-

trodeposition to electromechanical systems," ECS Trans. **97**, 485–490 (2020).

- L. E. Bodrova, S. Y. Melchakov, A. B. Shubin, and E. Y. Goyda, "Smart-microstructures of composites for electrical contacts with frameless packing of Cr and W in copper," Trans. Nonferr. Met. Soc. China (English Edition) 31, 2773–2786 (2021).
- L. E. Bodrova, S. Y. Melchakov, E. Y. Goyda, and A. B. Shubin, "Synthesis of arc-resistant W70Cu30 composite alloy with frameless placing of thin-dispersed tungsten phase," Inorg. Mater.: Appl. Res. 11, 495–502 (2020).
- N. Ray, B. Kempf, T. Mützel, L. Froyen, K. Vanmeensel, and J. Vleugels, "Effect of WC particle size and Ag volume fraction on electrical contact resistance and thermal conductivity of Ag–WC contact materials," Mater. Design 85, 412–422 (2015).
- Y. Wang, L. Zhuo, and E. Yin, "Progress, challenges and potentials/trends of tungsten-copper (W-Cu) composites/pseudo-alloys: fabrication, regulation and application," Int. J. Refr. Met. Hard Mater. 100, 105648 (2021).
- O. Güler, T. Varol, U. Alver, and S. Biyik, "The wear and arc erosion behavior of novel copper based functionally graded electrical contact materials fabricated by hot pressing assisted electroless plating," Adv. Powder Technol. 32, 2873–2890 (2021).
- S. Grigoriev, E. Gershman, I. Gershman, A. Mironov, and P. Podrabinnik, "Microstructural studies of the copper-based coating obtained by cold gas-dynamic spraying for the restoration of worn-out contact wires," Coatings 11, 1067 (2021).
- D. A. Romanov, V. E. Gromov, and S. V. Moskovskii, "Laws of formation of structure and properties of electroexplosive coatings on the electrical contacts of powerful electrical networks," in *Anthology of Strength and Plasticity of Metals and Alloys under External Energy Action. Ser. Fundamental Problems of Modern Materials Science*, Ed. by V. E. Gromov (SibGIU, Novokuznetsk, 2018), pp. 39–61.
- D. A. Romanov, S. V. Moskovskii, V. E. Gromov, K. V. Sosnin, and A. D. Filyakov, "Structure and electroerosion resistance of an Ag–CuO coating fabricated by electroexplosive spraying on copper electrical contacts," Deform. Razrushenie Mater., No. 6, 22–25 (2019).
- 15. D. A. Romanov, V. V. Pochetukha, and V. E. Gromov, "Structure and properties of electroerosion-resistant coatings of the WN–WC– $W_2C_{0.84}$ –Ag system fabricated by a combined method," Deform. Razrushenie Mater., No. 8, 8–12 (2021).
- 16. T. Rautio, A. Hamada, J. Kumpula, A. Yärvenpää, and T. Allam, "Enhancement of electrical conductivity and corrosion resistance by silver shell copper core coating of additively manufactured AlSi10Mg alloy," Surf. Coating Technol. 403, 126426 (2020).

Translated by K. Shakhlevich