

# MODERN COMPOSITE MATERIALS FOR SWITCHING AND WELDING EQUIPMENT

## Information 2. Application of high-rate vacuum evaporation methods for manufacturing electric contacts and electrodes

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The paper presents the method of electron beam vacuum evaporation and condensation for the most promising technologies of manufacturing modern composite materials, used in welding and switching equipment. This method currently is one of the components of the technological process of producing thin (up to 5  $\mu\text{m}$ ) films for radio engineering, microelectronics, computer engineering, etc., as well as thick (more than 5  $\mu\text{m}$ ) films-condensates widely applied as effective protective and wear-resistant coatings. Described are the results of scientific and production activity on introduction into industry of technologies of deposition of thick films based on copper and refractory metals (molybdenum, tungsten, chromium) with additives of REM and other metals (yttrium, zirconium) on the surface of electric contacts and electrodes. Proceeding from the results of trials performed in more than 54 enterprises of Ukraine, Russia, Georgia, Rumania, Poland and PRC it was established that the developed materials are not inferior to silver-containing powder compositions in terms of serviceability, while being approximately 3 times less expensive than the latter. 57 Ref., 1 Table, 4 Figures.

**Keywords:** *composite materials, copper and refractory metals, welding and switching engineering, electron beam evaporation, condensate films, serviceability*

Development of physico-chemical fundamentals of creating new materials is the objective need of engineering and social advance of society. Without it, it is impossible to make significant progress in any of the important fields of science and technology. Based on estimates of US experts, in the next 20 years 90 % of modern materials will be replaced by fundamentally new ones that will lead to technological revolution in practically all the industrial sectors [1, 2]. One of progressive directions of development of principally new materials with preset properties is high-rate EB evaporation and condensation of metallic and non-metallic materials in vacuum. Evaporation and subsequent condensation of materials in vacuum is a relatively new direction in materials science [3].

At present, none of the engineering fields related to material producing and processing can do without the EB technology. This is accounted for by the highest efficiency of the electron beam, compared to other known concentrated energy flows (laser, plasma). The electron beam has the highest coefficient of energy absorption. Ranges of power and energy concentration in the beam are significant (electron beam power of 1 MW and more). In this connection, material heat-

ing up to specified melting and evaporation temperatures occurs at very high rates [4].

EB evaporation and condensation in vacuum are one of the components of the technological process of producing thin (up to 5  $\mu\text{m}$ ) films for radio engineering, microelectronics, computer engineering, etc. [5], as well as thick (more than 5  $\mu\text{m}$ ) films, applied as effective protective and wear-resistant coatings [6–10].

A promising avenue is development of multi-component coatings designed for increasing erosion resistance of electric contacts of switching devices. Scientific and production experience gained at development of coatings from copper-based alloys alloyed with tin, chromium, aluminium, nickel and titanium is generalized in monograph [11].

Applicability of high-strength films of Cu–0.5Al<sub>2</sub>O<sub>3</sub> system (here and furtheron — wt.%) as coatings for electrical engineering products is noted in [12]. It is established that vacuum-deposited coatings are greatly superior to the respective electroplated ones by the level of wear resistance and, particularly, temperature stability.

Despite the obvious advantages, vacuum coatings are not always economically justified, as the coeffi-

cient of vapour utilization usually does not exceed 10–15 %. At the same time, the differences in component vapour pressure lead to insurmountable difficulties at evaporation from one source of copper- or silver-based materials with additives of refractory metals (tungsten, molybdenum, tantalum, niobium, zirconium) in a particular proportion, corresponding to the composition of modern electric contact materials.

It is known that powder metallurgy methods are the traditional ones for manufacturing composite materials (CM) for electric contacts. Technological features of producing materials for electric contacts, their service characteristics and applications are described in [13–20]. The latest achievements in this field of materials science are generalized in [21].

Despite a wide selection of materials for switching and welding engineering, the problem of development of highly reliable CM still has not been fully solved, as the requirements made of contact material, depend on the type of switching device and change with its upgrading and replacement by new equipment. Similar requirements are in place also for CM applied in welding engineering. These requirements can be met by materials, characterized by optimized structure and respective set of properties, providing formation of «secondary structure» with increased electroerosion resistance, service life and reliability in the working layer.

The structural factor has a decisive influence on service properties of materials of electric contacts and electrodes. Increase of CM dispersity in Ag–Me, Ag–MeO system promotes lowering of plasma flow intensity, and increase of electroerosion resistance of contacts and electrodes from these materials [22].

Evaporation and condensation processes allow engineering materials on atomic-molecular level and, as a result, precisely controlling their dispersity. In this connection, application of high-rate EB evaporation and subsequent condensation of metals in vacuum to produce bulk condensed CM for electric contacts and electrodes is of considerable scientific and practical interest. Condensed from the vapour phase CM based on pure metals and their alloys, oxides, carbides, borides, CM which are of dispersion-strengthened, microlaminate and microporous types of 0.1 to 2.0 mm thickness, have been studied since 1970s at PWI [23], Royal Aviation Research Institute of UK Ministry of Defense [24], and a number of other research laboratories [25]. Results of these studies were generalized in [26, 27]. Until recently, however, there has been no information about industrial production of such materials as individual structural elements of assemblies, instruments and mechanisms.

Of greatest interest is development and wide introduction into different engineering sectors of CM condensed from the vapour phase for contacts and electrodes, not containing any noble metals. It should be

noted that materials, produced by powder metallurgy methods without noble metals, are widely accepted in manufacture of electrodes and contacts of switching devices. Powder CM for these contacts and electrodes contain 20 to 80 % of the refractory component (as a rule, these are tungsten, molybdenum and chromium), while copper is the low-melting component. Nickel and cobalt can be the technological additives, and some oxides, boron and other elements can be the functional additives. Powder CM with 50 and 70 % content of refractory phase are mainly used in industry [15, 28].

At application of contacts and electrodes from CM of W–Cu system the oxidation products most often are  $WO_3$  and  $Cu_2O_3$  oxides [16, 29]. Their specific electric resistance varies in rather broad ranges: for  $WO_3$  from 1 (at strong deviation) to  $1 \cdot 10^{12}$  Ohm/cm (at stoichiometric composition), for  $Cu_2O$  — from  $10^3$  to  $10^{10}$  Ohm/cm.

At current switching in air, such processes are observed also in the working layer of contacts from Mo–Cu pseudoalloys. Molybdenum and copper are mutually partially soluble [30], while their oxides interact and form resistant compounds ( $CuMoO_4$ ,  $Cu_3Mo_2O_9$ ) [31, 32]. At temperature above 700 °C, a low-melting eutectic forms in  $MoO_3$ – $Cu_2O$  system. It is found that the oxide film, having the composition of eutectic of this system, spreads easily over the contact surface, filling its unevenness [31, 32]. The film has weak adhesion to the base and its delamination from the contact surface after solidification promotes the «self-cleaning» effect and lowering of the level of the contact pair transient resistance [28].

When solving the problem of producing from the vapour phase the composites for electric contacts and electrodes, a number of scientific and applied studies on development CM based on copper, molybdenum, tungsten and chromium were performed, which included:

- selection of alloying elements and development of the processes of their addition to the copper matrix to produce two- and multicomponent CM based on copper with improved physico-chemical, mechanical and corrosion characteristics;
- investigation of the influence of interphase interaction in copper–refractory component system, material, temperature and substrate roughness on CM structure and properties;
- analysis of variation of CM structure and properties, depending on chemical composition of initial (evaporated) components and their deposition rate, substantiation of separating layer material selection;
- studying the influence of alloying phases on increase of copper evaporation rate and determination of optimum composition of alloying additives;
- conducting integrated studies of the structure, physico-chemical and mechanical properties of grad-

| Material | Chemical composition, wt. %    | Density, g/cm <sup>3</sup> | Specific electric resistance, $\mu\text{Ohm}\cdot\text{m}$ | Hardness $HV$ , MPa | Mechanical properties |              |   |              |
|----------|--------------------------------|----------------------------|--|---------------------|-----------------------|--------------|---|--------------|
|          |                                |                            |  |                     | Before annealing      |              | After annealing in vacuum (900 °C, 1 h) |              |
|          |                                |                            |  |                     | $\sigma_p$ , MPa      | $\delta$ , % | $\sigma_p$ , MPa                        | $\delta$ , % |
| DSMC-1   | Cu–(0.05–0.1)(Zr, Y)–(3–5)Mo   | 8.9–9.0                    | 0.021–0.022  | 1000–1500           | 300–430               | 10.3–7.3     | 295–420                                 | 17.6–9.3     |
| DSMC-2   | Cu–(0.05–0.1)(Zr, Y)–(5.1–8)Mo | 9–9.05                     | 0.022–0.024  | 1500–1650           | 440–630               | 7.25–3.40    | 425–600                                 | 9.45–4.90    |
| DSMC-3   | Cu–(0.05–0.1)Zr, Y)–(8.1–12)Mo | 9.05–9.1                   | 0.024–0.028  | 1650–1800           | 635–785               | 3.25–1.80    | 605–730                                 | 4.85–3.90    |

ed two- and multicomponent Cu-based CM produced on stationary and on rotating substrates;

- conducting integrated corrosion studies of CM and determination of mechanisms of corrosion processes running;

- issuing recommendations on corrosion-resistant Cu-based CM, condensed from the vapour phase, development of commercial equipment and their manufacturing technologies.

Main results of conducted fundamental, scientific and applied research are set forth in [33–35] and are generalized in [36]. Results of performance of the above-mentioned work can be described as follows. Physico-chemical principles of designing Cu-based CM condensed from the vapour phase were defined, which enabled transition from laboratory studies to their broad industrial application. Integrated studies of the structure, physico-chemical, mechanical and service properties of Cu–Mo, Cu–W, Cu–Cr, (CuZrY)–Mo CM in the range of up to 50 % concentrations of refractory components were performed; comprehensive studies of corrosion resistance of two- and multicomponent CM were conducted and their corrosion resistance points were calculated; formation of oversaturated solid solutions on submicron level in Cu–W, Cu–Mo, Cu–Cr CM was established, that leads to laminated structure formation as a result of their decomposition. It was proposed for the first time to alloy the copper matrix with zirconium and yttrium with their total content of up to 0.1 % in CM, by copper evaporation from Cu–Zr–Y alloy through intermediate pool, that provided simultaneous increase of CM corrosion

resistance and copper evaporation rate 2 to 3 times, and it was experimentally shown that Cu–0.1(Zr, Y)–(8–12)Mo and Cu–0.1(Zr, Y)–(0.3–0.34)Cr–(8–12)Mo CM condensed from the vapour phase are bulk nanocrystalline systems.

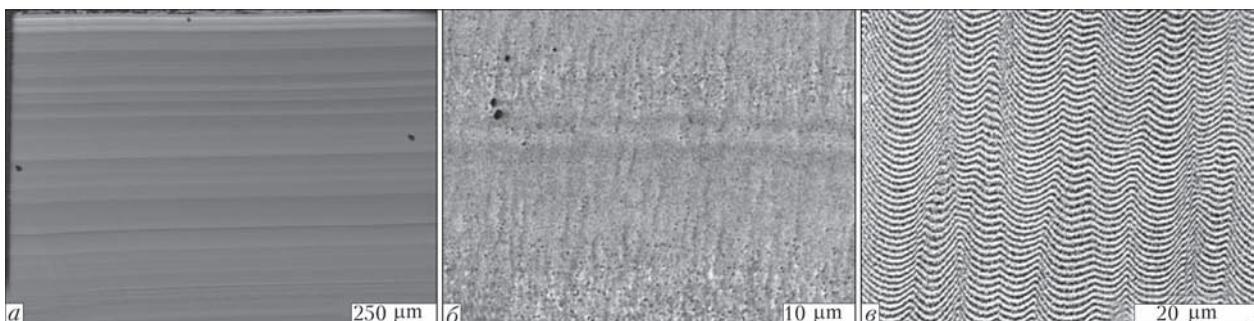
**Cu–Z–Y–Mo CM condensed from the vapour phase.** Cu–Zr–Y–Mo systems have become the most widely applied [33, 36, 37].

The Table gives chemical composition and main physico-chemical properties of the above materials.

New composites, called dispersion-strengthened materials for electric contacts (DSMC), are certified in keeping with Ukrainian standards [38, 39]. Chemical composition and technology of their manufacturing are protected by patents of Ukraine and Russian Federation [40–42].

Cu-, Mo- and W-based CM, condensed from the vapour phase, are characterized by a laminated structure with layer hierarchy on macro-, micro- and submicron levels (Figure 1).

Lamination is weakly pronounced at small concentration of molybdenum (up to 7–8 %) and tungsten (up to 4 %). With increase of refractory component content, the image contrast is enhanced that points to their greater lamination due to various factors. Presence of lamination on the macrolevel is due, most probably, to development of electric microbreakdowns, arising at high-rate evaporation of initial commercially pure components (rate of copper deposition on a rotating steel substrate of 1000 mm diameter reaches 60–70  $\mu\text{m}/\text{min}$ , that of molybdenum — 6–8  $\mu\text{m}/\text{min}$ ). Lamination on the microlevel is due to impurities,



**Figure 1.** Laminated structure of Cu- and Mo-based CM on macro- (a), micro- (b) and submicron (c) level

present in the initial (evaporation) materials. Layer formation at submicron level is associated with formation of oversaturated solid solutions, which, while decomposing, form the respective microlayers [36]. Switching testing showed that in such a graded laminated nanomaterial changes of layer chemical composition essentially limit the zone of discharge thermal impact. In a number of types of switching devices and instruments, smaller changes of working layer of contacts and electrodes and increase of erosion resistance are observed, compared to analogs produced by powder metallurgy.

The most effective fields of DSMC application are city transport (contacts, used in city trams, trolleybuses, metro trains; intercity electric transport, diesel locomotives, electric trains; lift facilities (passenger and cargo lifts); port, ship cranes and other hoisting mechanisms; electric trolleys of all types; mining equipment; industrial and household electric appliances, containing relays, starters, contactors, knife switches, etc.).

General view of breaking contacts, made with application of DSMC, is shown in Figure 2.

DSMC-3 have become applied by industry as electrodes for welding brass strip to copper wire in capacitor spot welding machines of TKM 15 and TKM 17 type. Results of electrode testing in «Shostka Kazenny Zavod «Impuls» enterprise are given below.

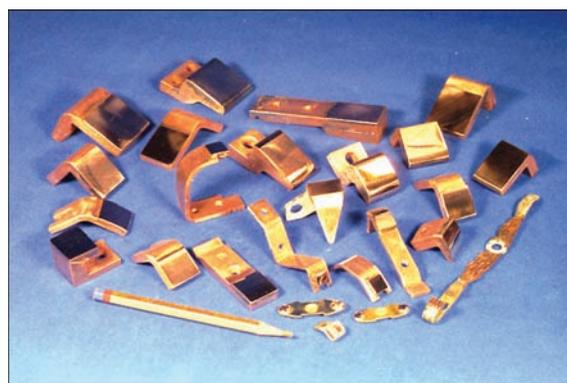
Actual operating life of electrodes made from DSMC-3 (scheduled life of 100000 cycles) is as follows:

- 1 (upper electrode in TKM 15) — 105,000;
- 2 (lower electrode in TKM 15) — 120,000;
- 3 (upper electrode in TKM 17) — 110,000;
- 4 (lower electrode in TKM 15) — 125,000.

Electrodes manufactured from DSMC-3 meet all the requirements made of electrodes used in capacitor spot welding machines of TMK 15 and TKM 17 type.

A fundamentally new application of DSMC-3 was their use as electrodes for live tissue welding [43]. Manufacture of nozzles from these materials for supersonic electric arc spraying was mastered. Replacement of beryllium bronze by DSMC is promising. Unlike bronze, CM of DSMC grade do not lose their strength right up to heating temperature of 900 °C. Above-mentioned CM can also be used as spring alloys with high electric conductivity, alloys resistant to radiation swelling, and as coatings for mirrors in power metal optics [36].

**Composite materials condensed from the vapour phase.** *Cu-Cr-Zr-Y-Mo CM.*  $\text{Cu-(0.2-0.41)Cr-(0.05-0.1)(Zr, Y)-(8-12)Mo}$  CM (MDK3Kh grade) are an optimized variant of DSMC-3. It was experimentally confirmed that  $\text{Cu-(0.05-0.1)(Zr, Y)-(8-12)Mo}$  CM are bulk nanocrystalline materials with average grain dimensions of 80 nm for copper and 10 nm for molybdenum. Owing to additional alloying with chromium, MDK3Kh feature 1.5 to 2 times higher corrosion resistance,



**Figure 2.** General view of typical breaking contacts made with application of DSMC

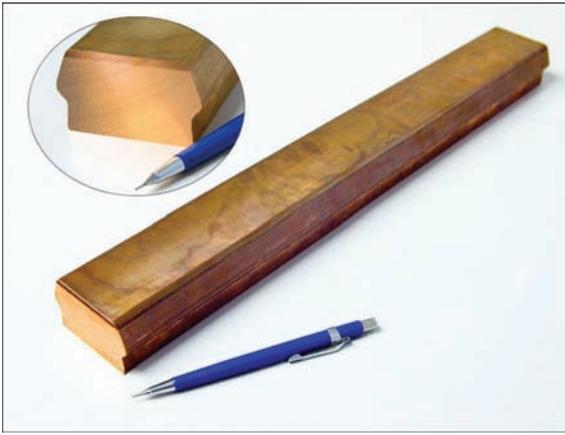
compared to DSMC-3 with preservation of the level of physico-mechanical properties of the latter [44]. They are, mainly, used for manufacturing breaking contacts of mining equipment, where humidity reaches more than 80 % and  $\text{CO}_2$  and  $\text{SO}_3$  aggressive gases are present, in particular, in Smolinskaya and Ingulskaya uranium mines (Ukraine).

*Cu-Zr-Y-C CM.*  $\text{Cu-(0.05-0.1)(Zr, Y)-(0.3-0.6)C}$  CM (MDK3S grade) are used on industrial scale for manufacturing sliding contacts [45, 46]. Pantographs from these materials (Figure 3) have become applied in locomotives, pulling trolleys with copper ore at Copper-Ore Works (Lublin, Poland).

*Cu-(0.05-0.1)(Zr; Y)-W CM.* Structure, physico-chemical, mechanical and service properties of composites with up to 50 % W content are described in detail in [47-50]. Cu- and W-based composite materials are traditionally used as high-current electric contacts in oil circuit-breakers. Recently they are also becoming applied in some types of vacuum devices. In particular,  $\text{Cu-(0.05-0.1)(Zr, Y)-(32-36)W}$  CM, condensed from the vapour phase, have become applied in industry for manufacturing contacts of oil circuit-breakers of RNO and RNT-17 type. The above materials have successfully passed pilot industrial testing in vacuum arc chutes MVK-440, used, mainly, in coal mines [51].

*Cu-(0.05-0.1)(Zr; Y)-Cr CM.* Influence of technological factors on the structure and mechanical properties of  $\text{Cu-Zr-Y-Cr}$  CM condensed from the vapour phase with up to 60 % Cr content is described in [52].  $\text{Cu-Cr}$  CM with 35-50 % Cr are widely applied for manufacturing contacts of vacuum arc chutes.

Possibility of applying condensed CM of this system is due to the features of chemical composition and morphology of «secondary» structure formed on contact working surface. Under non-equilibrium conditions of the arc discharge, mutual solubility of copper and chromium in the working layer rises, and solid solution decomposition with dispersed structure formation takes place.  $\text{Cu-Zr-Y-Cr}$  condensates at this chromium content have a laminated structure on



**Figure 3.** General view of sliding contacts made from MDK3S material

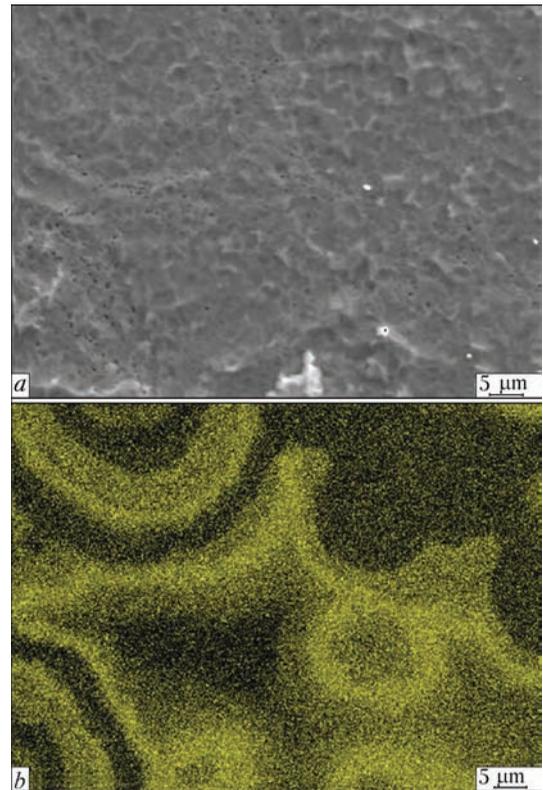
macro-, micro- and submicrolevels. Lamination of the latter two levels is attributable to anisotropy of normal grain growth, promoting formation of «columnar» structure within several layers of the condensate, in which a structure with polygonal grain shape (Figure 4, *a*) and indications of solid solution delamination (Figure 4, *b*) forms in the section of the layer, normal to the columns, under the impact of temperature and time.

Change of Vickers hardness, depending on chromium content, is of a linear nature; in the concentration range of 35–50 % Cr, hardness varies in the range of 2069 to 2503 MPa. At tensile testing, ultimate strength rises to 550 MPa, the CM, however, has zero ductility. Cu–Zr–Y–Cr CM are becoming accepted for manufacturing arc chute contacts [53, 54].

CM condensed from the vapour phase feature several advantages: they are produced in one process cycle, they are less expensive than their analogs produced by powder metallurgy methods (1.5 to 1.7 times) and essentially (4 times) less expensive than the materials of silver-containing contacts. In terms of their serviceability, condensed CM are not inferior to materials based on silver-containing compositions. They are readily treatable by cutting, grinding, drilling; are easily soldered by any of the known soldering processes, with application of standard silver-containing and non-silver solders. Industrial certified EB equipment has been developed for manufacturing CM condensed from the vapour phase [55, 56], which allows manufacturing up to 12 tons per year of composites of various composition. During the period of 1995 to 2015, more than 15 tons of CM have been manufactured, from which about 1.6 mln contacts and electrodes of 386 typesizes have been produced [57].

## Conclusions

Industrial EB equipment has been developed for producing copper-, molybdenum-, tungsten- and chromium-based CM, condensed from the vapour phase,



**Figure 4.** Microstructure of Cu–Zr–Y–Cr CM with 35–50 % Cr in secondary electrons (*a*) and in copper X-rays (*b*)

which are used in manufacture of electric contacts and electrodes.

Testing conducted in more than 54 enterprises of Ukraine, Russia, Georgia, Rumania, Poland and PRC showed that, in terms of serviceability, the developed materials are not inferior to silver-containing powder compositions, while being approximately 3 times less expensive than the latter.

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