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PHYSICAL AND ELECTRICAL PROPERTIES OF SILVER-MATRIX COMPOSITES REINFORCED WITH VARIOUS FORMS OF REFRACTORY PHASES

This paper presents technological trials aimed at producing Ag-W, Ag-WC, Ag-W-C and Ag-WC-C composite contact materials and characterizing their properties. These materials were obtained using two methods, i.e. press-sinter-repress (PSR) at the refractory phase content of less than 30% by weight as well as press-sinter-infiltration (PSI) at the refractory phase content of ≥50% by weight). The results of research into both the physical and electrical properties of the outcome composites were shown. They include the analysis of the influence of the refractory phase content (W or WC) on arc erosion and contact resistance changes for the following current range: 6 kA_{max} in the case of composites with a low refractory phase content, 10 kA_{max} in the case of composites with the refractory phase content of ≥50% by weight.

Keywords: composite materials, electrical contacts, arc erosion, contact resistance

1. Introduction

Both phase composition and structure of composites has a major impact on the properties of materials and their applicability [1-7]. Contact materials carrying high electric current in variable bonding conditions can serve here as an example. Undoubtedly, this has a significant influence on the contact wear mechanism. Resistance, the amount of heat generated for the switch throughput when a contact or a contact pair is closed, as well as arc erosion resistance when they are being opened are all dependent on the phase composition and structure of composite contacts [8-11]. Direct contact-point surfaces are the most exposed to the high thermal energy of the electric arc. Therefore, refractory wolfram or wolfram carbide are used as phases increasing the material's resistance to the effect of the pulse, high temperatures.

Most frequently, contact materials are produced using powder metallurgy methods, and their chemical composition determines the manner in which they are obtained. Depending on the refractory phase content, the following two production methods were selected:

– press-sinter-repress (composites with the refractory phase content of less than 30 wt.%),
– press-sinter-infiltration (composites with the refractory phase content of ≥50 wt.%).

In recent years, attempts have been made to make refractory phases composites Me (Ag, Cu) using new methods, eg. SPS (Spark Plasma Sintering) [12] and LAM (Laser Additive Manufacturing) technologies [13,14].

After performing multiple numbers of switching cycles with electric arc discharge, two types of structures can be identified:

– exposed primary structures remaining after the surface layer's melting and evaporation,
– secondary structures formed when the electric arc goes out, appearing as solidified drops of arc plasma components.

Skeletons of WC or W crystallites, resintered once silver had evaporated, are classified as belonging to a group of these structures. To date, a coherent experimentally confirmed theory of electric current flow through a composite material has not been developed. Research works, in this case, are particularly time-consuming. They include the composite contact tips formation stages, tests in specific control systems and analyses of a wide spectrum of structure and phase scanning detection cycles lasting long hours. In this work, the production methods of Ag-W, Ag-WC, Ag-W-C and Ag-WC-C contact materials are presented. Results of research into the physical and electrical properties of these composites and the influence of the refractory phase content in these composites on the specified properties are shown.

2. Experimental

The following powders were used to produce Ag-W, Ag-WC, Ag-W-C and Ag-WC-C composites:

– Handy&Harman Ag (LCP1) silver with the average grain size of 1.5 μm,

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– HC Starck WC wolfram carbide with the average grain size of 2.5 µm,
– HC Starck W wolfram with the average grain size of 2.5 µm,
– Aldrich C graphite with the average grain size of 3.1 µm.

The composite materials obtained employing the solid-phase sintering method were composed of Ag and W or Ag and WC powder mixtures. Mouldings were formed with a hydraulic press using the pressure of 196 MPa with an additional Ag powder layer (0.2 mm) to enhance weldability. The sintering process was carried out in a furnace with dry hydrogen atmosphere at the temperature of 1173 K (below silver's melting temperature). The sintering process lasted 60 minutes. The samples were repressed after sintering using the pressure of 883 MPa.

First of all, in the case of infiltration-based composites, powder mixtures were prepared. W and WC mouldings were pressed from these mixtures using the hydraulic press. The pressing pressure of 196 MPa was chosen. The mouldings were sintered for 40 minutes in a furnace with dry hydrogen atmosphere at the temperature of 1373 K. The sintering process resulted in obtaining porous skeletons from the refractory phase, which were next saturated with silver. The process was carried out at the temperature of 1423 K, for 30 minutes in dry hydrogen atmosphere. After machining, getting contact tips dimensions, the mounting side was coated with the AgCu28P1 alloy in conditions: dry hydrogen atmosphere at 963 K temperature.

The list of the produced materials can be found in Table 1.

TABLE 1

Types of analysed samples

Ordinal	Material	Samples chemical composition [%w]				Production method
		Ag	W	WC	C	
1	Ag-WC	90	—	10	—	PSR
2	Ag-WC	80	—	20	—	PSR
3	Ag-WC-C	80	—	19.5	0.5	PSR
4	Ag-W-C	80	19.5	—	0.5	PSR
5	Ag-W	50	50	—	—	PSI
6	Ag-W	25	75	—	—	PSI
7	Ag-WC	40	—	60	—	PSI
8	Ag-WC	30	—	70	—	PSI

3. Results

3.1. Physical properties

The hydrostatic method was employed to determine density. Samples' hardness was measured using the Vickers test at the load of 90.81 N with the Emcotest DuraScan hardness testing machine. Ten measurements were made for each sample.

Table 2 summarizes results gathered in the area of the physical properties of the analyzed materials.

The run experiments prove that for the majority of samples obtained using the solid-phase sintering method and densification, as well as those produced following the infiltration method, densities are comparable to theoretical densities. The results of the Vickers hardness test show a significant increase of hardness observed when the refractory phase content in a composite is raised. For comparison, wolfram, wolfram carbide and silver hardness is 310 HV, 900-1600 HV and 25 HV respectively.

Microstructure images from the Axiovert 40 MAT optical microscope are presented in Fig. 1 and 2. They show a uniform distribution of the refractory phase in the silver matrix.

TABLE 2

Physical properties of samples

Ordinal	Material	Density γ [gcm^{-3}]	Density γ_O [gcm^{-3}]	γ/γ_O [%]	Hardness HV 10
1	Ag-WC10	10.76	10.86	99.1	82.0
2	Ag-WC20	11.08	11.24	98.6	92.0
3	Ag-WC19,5-C0,5	10.87	11.00	98.8	87.6
4	Ag-W19,5-C0,5	11.26	11.88	99.6	95.8
5	Ag-W50	13.50	13.60	99.3	115.0
6	Ag-W75	15.68	15.96	98.2	195.0
7	Ag-WC60	12.80	13.07	97.9	270.0
8	Ag-WC70	13.30	13.63	97.6	310.0

γ – sample density; γ_O – theoretical density

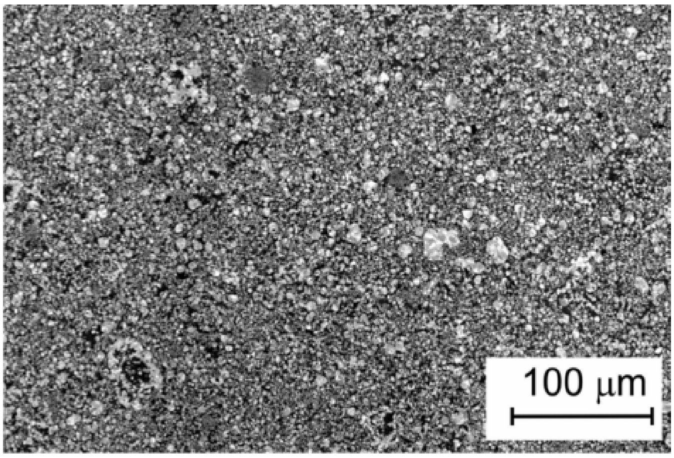


Fig. 1. Microstructure of Ag-WC19.5-C0.5 composite after PSR process

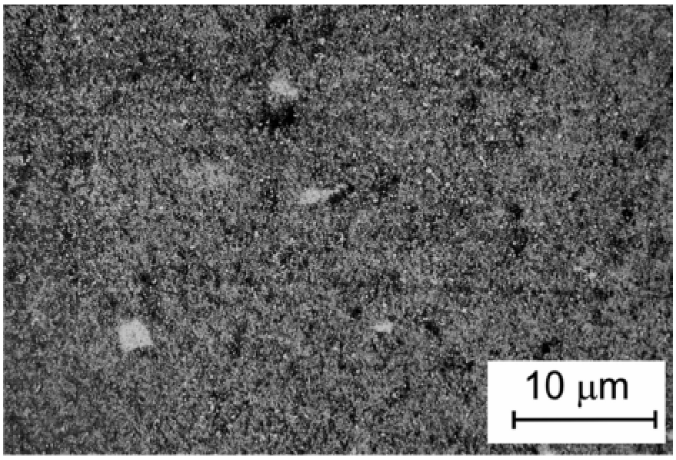


Fig. 2. Microstructure of Ag-WC70 composite obtained using PSI process

The way in which very fine, dark wolfram carbide grains are distributed against the bright silver matrix demonstrates that the composite structure is homogeneous.

A similarly homogeneous structure (Fig. 2) is observed for the composites gathered fine WC particles in the silver matrix. On the microstructure some silver areas without WC phase were observed (light areas).

3.2. Electrical properties of contact tips

Electrical analyses included arc erosion and contact resistance measurements in model test conditions. As a result of arc erosion of contacts, observed when switching off high currents, the contact surface is worn out. When the electric arc occurs, thermal erosion phenomena lead to contact mass loss, surface degradation and change of the surface layer properties, including higher contact resistance. Studies conducted so far and focused on the erosion of contacts made of assorted metals and composite materials, such as Ag-Me, Ag-MeO and Ag-C, under contact polarization conditions showed that for currents higher than 1 kA anode mass loss is usually greater than in the case of a cathode [7,15,16]. When compared with the initial state, for the aforesaid composite materials and some current values cathode mass gain was observed instead of loss. This is caused by the material's transport from the anode to the cathode to a degree higher than its decrement in the cathode. In all cases, a part of the anode material and the cathode material is scattered outside the contacts. In the case of high-current switches, the dissipated liquid metal drops are deposited on the surface of insulating elements, thus reducing a switch's durability [16].

Electrical analyses were performed for the contacts using a computer-operated testing system, a detailed presentation of which can be found in the work [17]. The erosion tests in the case of contacts made of composites obtained using solid-phase sintering (i.e. Ag-WC10, Ag-WC20, Ag-WC19.5-C0.5, Ag-W19.5-C0.5) were performed for polarized contacts switching off the half-wave current of 6 kA_{max} (Q = 34 C). The contacts' opening time was chosen in such a way as to get the arc time of around 8 ms. The sample thickness was 2.5 mm, whereas diameter equalled 10 mm.

Similarly, erosion of the contacts produced using the infiltration method (i.e. Ag-W75, Ag-W50, Ag-WC60, Ag-WC70) was analysed. The test stand enabled the flow of the half-wave current of 10 kA_{max} (Q = 55 C) through the contacts and time of 8 ms. The samples were 2.5 mm thick and 15 mm in diameter. Weight loss as a function of the number of switching operation measurements were carried out for all contacts and are presented in the form of erosion characteristics. The above-mentioned test current values were selected so as to provide a basis for determination of the contact erosion in switches with the rated direct currents of up to 630 A, operating in short circuit conditions. Exemplary characteristics for Ag-W50 and Ag-WC60 composite contacts are presented in Fig. 3. Based on these, arc erosion diagrams for the analyzed composites were collected in Fig. 4 and 5.

Erosion tests for the composite materials at the current of 6 kA_{max} (Fig. 4) proved that the Ag-WC19.5-C0,5 and Ag-W19.5-C0.5 materials are the most resistant to erosion. Erosion characteristics for these two materials are much alike. The contact mass losses are practically identical, only with a slight advantage of the anode. It turned out that the cathode is the system element that wears out the most for the Ag-WC10 and Ag-WC20 materials. Erosion characteristics presented in the form of diagrams in Fig. 5, at the current of 10 kA_{max}, show that the contact that is the least durable is the anode for Ag-W and the cathode for Ag-WC. Further research into the interaction between the electric arc and the Ag-WC contact material, as well as the influence of the Ag-WC material on the arc nature is required in order to understand this effect.

It needs to be highlighted though that both Ag-WC60 and Ag-WC70 composites are highly resistant to arc erosion at high currents, and much more resistant than similar Ag-W composites. Slade provides examples of research focused on the Ag-W50 material and the analyses of the relation between contact erosion and current strength, as well as contact surface [8]. The analysis of the arc erosion and its changes indicates that it is a function of current intensity. If higher the current values at which the

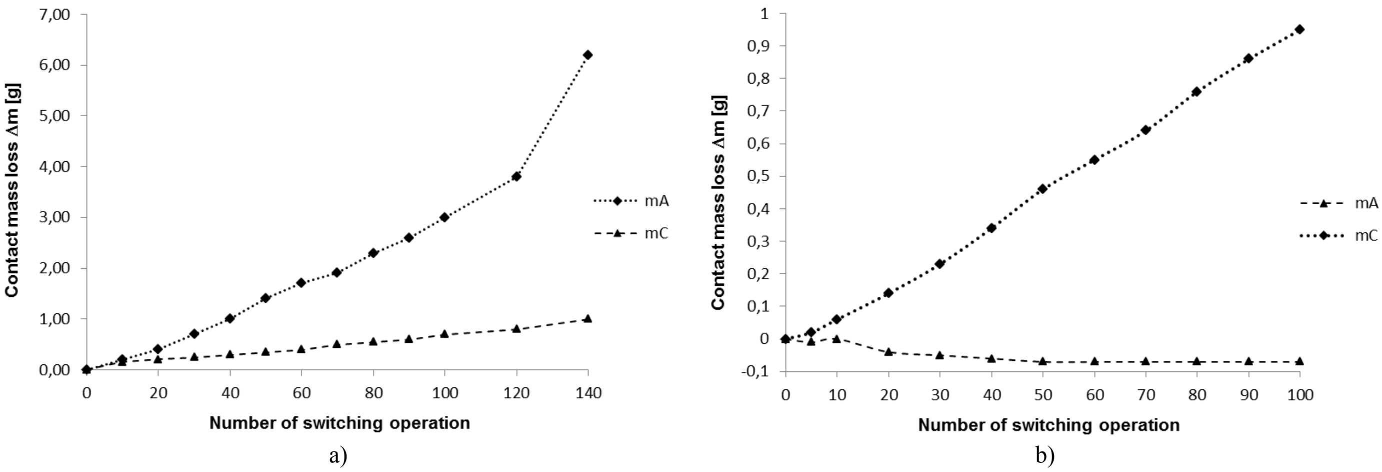


Fig. 3. Exemplary erosion characteristics as a function number of switching operations for contacts: a) Ag-W50; b) Ag-WC-60

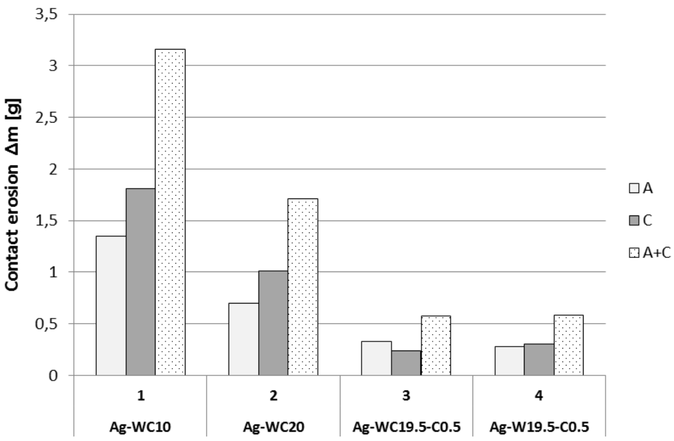


Fig. 4. Compilation of erosion test results for various composites at the current of 6 kA_{max}: 1 – Ag-WC10; 2 – Ag-WC20; 3 – Ag-WC19.5-C0.5; 4 – Ag-W19.5-C0.5
A – anode mass loss, C – cathode mass loss, A+C – total mass loss (anode and cathode)

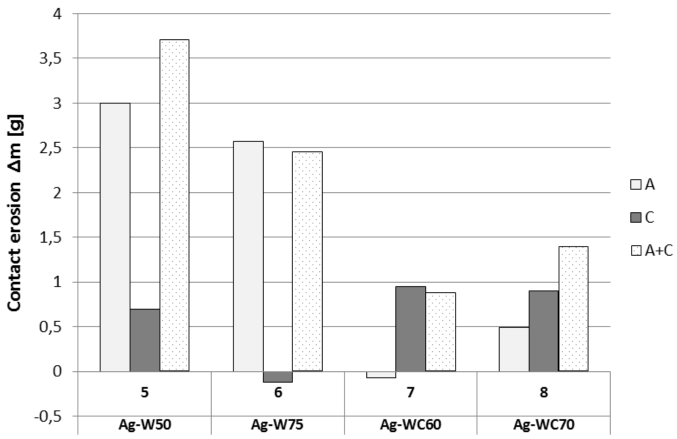


Fig. 5. Compilation of erosion test results for various composites at the current of 10 kA_{max}: 5 – Ag-W50; 6 – Ag-W75; 7 – Ag-WC60; 8 – Ag-WC70
A – anode mass loss, C – cathode mass loss, A+C – total mass loss (anode and cathode)

contacts were examined and the smaller contact surface, the contact erosion was more intense.

Contact resistance measurements were performed during the number of switching operation N = 40 at the current of 6 and 10 kA_{max} for PSR and PSI composites, respectively. The obtained results are gathered in Fig. 6 and 7.

The research works showed that the average resistance values for Ag-WC19.5-C0.5; Ag-W19.5-C0.5 (Fig. 6) did not exceed 0.1 mΩ. The resistance measurements taken at higher current values (10 kA_{max}) and for contacts with more considerable dimensions (Fig. 7) proved that resistance for contacts containing wolfram carbide was at least two times higher than for Ag-W based contacts, in the case of which relatively low resistance values for this type of composites were obtained.

4. Discussion

Erosion tests for Ag-WC60 contacts at high currents (10 kA_{max}), performed at the Department of Electrical Apparatus of Lodz University of Technology showed that the cathode is the contact system element that wears out the most [17]. On the other hand, anode mass increased slightly when compared to the initial mass or remained identical till the end of the test. Fig. 5 in the form of a diagram presents contact erosion for the current of 10 kA_{max} expressed as contact mass loss for the anode and the cathode respectively. Erosion characteristics for the analyzed Ag-WC70 composites vary from the Ag-WC70 composites in that anode erosion losses from the very beginning of the test were comparable to cathode losses. As a result, despite a bit less pronounced cathode erosion, the contact mass loss in total was bigger than for the Ag-WC70 contacts. It has to be accentuated though that the arc erosion resistance for both Ag-WC60 and Ag-WC70 composites at high currents is greater than for similar Ag-W composites [5]. Differences in the qualitative and quantitative relation between the anode and cathode erosion are particularly important when constructing contacts in the direct-current switches. The electrode determining contact durability at high currents is the cathode for the Ag-WC composite and the anode for the Ag-W composite

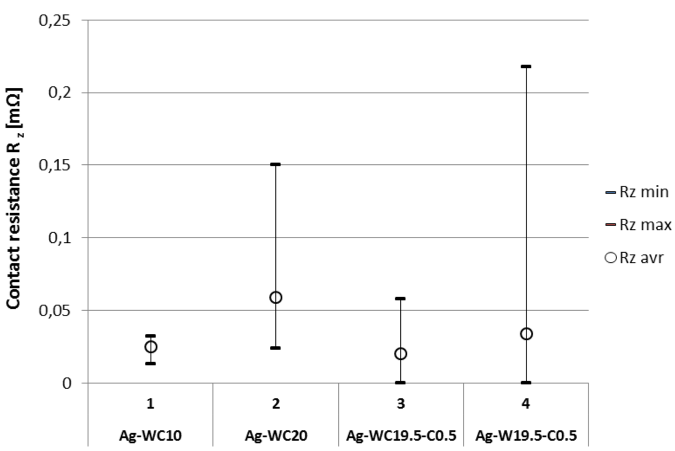


Fig. 6. Contact resistance measured during contact erosion tests at 6 kA: 1 – Ag-WC10; 2 – Ag-WC20; 3 – Ag-WC19.5-C0.5; 4 – Ag-W19.5-C0.5

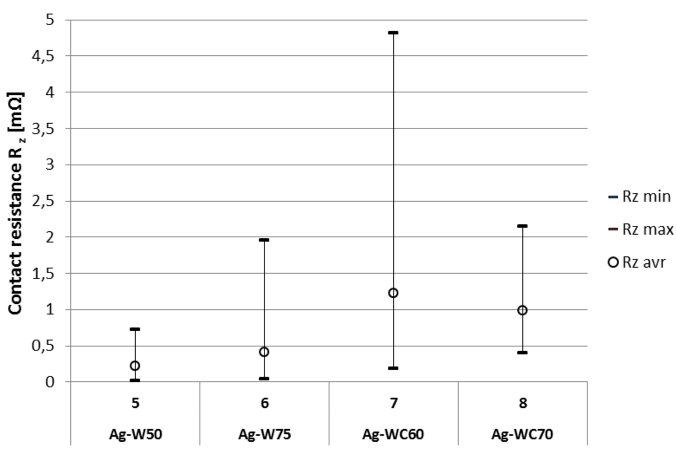


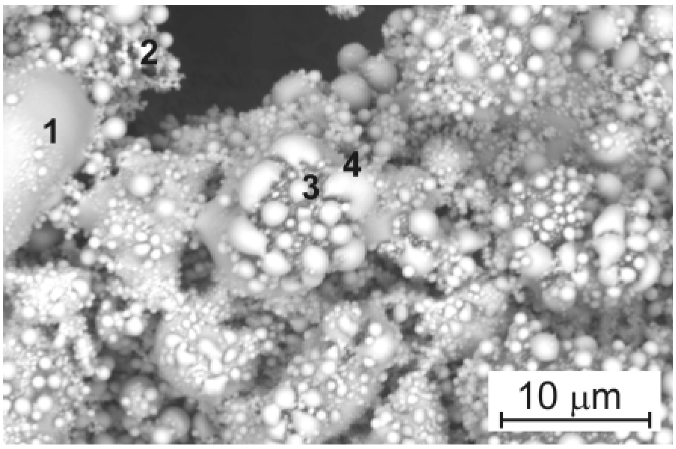
Fig. 7. Contact resistance measured during contact erosion tests at 10 kA: 5 – Ag-W50; 6 – Ag-W75; 7 – Ag-WC60; 8 – Ag-WC70

[17]. The erosion process at 6 kA_{max} is analogous for both Ag-WC10 and Ag-WC20 composites, and diagrams presenting it can be found in Fig. 3. Here, the less durable electrode is also the cathode.

Fig. 8 shows the surface of the Ag-WC10 contacts (anode and cathode) after operation in the electric arc.

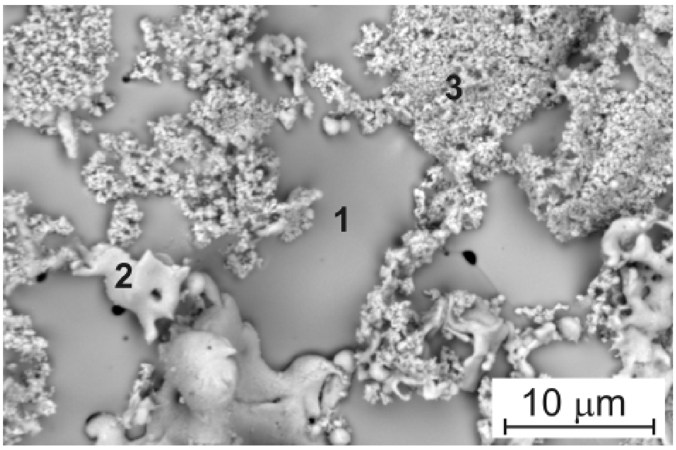
The microphotograph of the anode surface (Fig. 8a) clearly shows silver drops of various sizes. The larger drops (1) represent silver melted in the arc area, whereas numerous tiny drops (3, 4) on both WC substrate and larger drops are most probably the material originating from arc plasma. Silver is deposited in the form of fine, round droplets in spaces which are most likely covered with a discontinuous carbon layer, preventing wetting. Fig. 8 shows areas with solidified silver (1) and partially melted wolfram (2). In addition, one can notice thin crusts of the sintered WC crystallites (3). In the case of the Ag-WC-C and Ag-W-C materials, erosion tests revealed that irrespective of the composite type, erosion characteristics (as a function of the number of switching operations) are similar, whereas mass losses are directly proportional to the number of switching operations, with the cathode and anode wearing out practically at the same pace [20]. Allen et al. [18] focused on the Ag-W-C and Ag-WC-C-type materials with a varying content of wolfram carbide, wolfram and graphite. They concluded their research stating that the erosion of the contact material is caused by no adhesion between material's phases and its being too brittle. The mass loss is more significant once the carbon amount is higher, while when there is more silver, it gets smaller. Moreover, there is a greater tendency for craters to form in the material structure whenever the carbon content is increased. Observation of the Ag80-WC19.5-C0.5 contacts affected by an electric arc (Fig. 9) in cross section shows clear degradation of the microstructure in the surface layer of around 200 μm thickness. In this layer one can recognize areas with melted silver or wolfram as well as structure discontinuities. Solidified metal drops are frequently loosely bound to the contact material and get chipped during next bonding attempts. As a result, contact mass losses, observed due to sprinkling of liquid metal drops and evaporation [20], are additionally becoming greater.

Analyses of the contact resistance changes at the currents of 6 and 10 kA_{max} (Fig. 6 and 7) proved that the higher the wolfram carbide content in a composite, the higher the resistance value. Besides, it can be noted that for a vast majority of composites the average resistance at higher currents is raised. In all probability this results from a higher degradation degree of contact surfaces, inextricably linked with the evaporation of a considerable amount of silver and the formation of oxide films with high specific resistance on the surface. Lindmayer et



Point	Chemical element content [wt%]		
	Ag	W	C
1.	96.66	2.19	1.15
2.	36.5	62.3	1.09
3.	93.24	4.77	1.99
4.	96.15	2.87	0.98

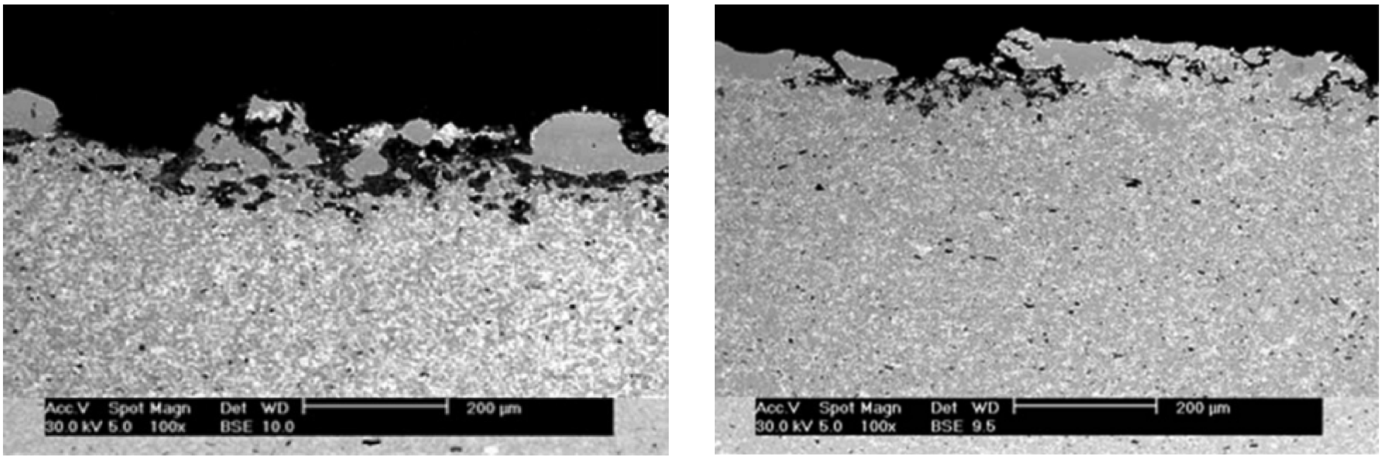
a)



Point	Chemical element content [wt%]		
	Ag	W	C
1.	95.56	3.99	0.45
2.	5.76	91.89	0.34
3.	32.60	66.62	0.78

b)

Fig. 8. Surface of Ag-WC10 contacts and local analysis of chemical composition: a) anode, b) cathode



a) b)

Fig. 9. Cross section of Ag80-WC19.5-C0.5 contacts after operation in electric arc: a) anode, b) cathode

al. [19] researched into erosion resistivity and raise of contact resistance in the Ag-W and Ag-WC materials with a differing chemical composition, at the current of 1000 A and voltage of 230 V. They found that contact resistance of the Ag-W materials changes at 1:1000. High contact resistance is due to the presence of wolfram and wolfram oxides in the surface layer.

5. Conclusions

Based on the presented analyses it can be stated that the wolfram carbide content in a composite exerts considerable influence on the nature of contact surface changes affected by an electric arc. In the case of the Ag-WC composite, as the temperature is raised upon exposure to the electric arc, in the 3073-3143 K temperature range one can observe a peritectic transformation of wolfram carbide (i.e. incongruent melting). Solid carbon is separated from wolfram carbide until WC is completely decomposed.

In composites with a low wolfram carbide content (10, 20% by weight) one can observe large silver areas with fine carbon crystallites on the contact surface, as a result of which contact resistance is slightly changed. When there is much more wolfram carbide in the composite (60, 70% by weight), widespread wolfram regions with significantly lower thermal conductivity than silver, are formed on the contact surface. Re-sintered layers and metals blooming over the contact surface are observed. Thus leading to the reduction of the contact area and, in consequence, increasing contact resistance [16]. Familiarity with the influence of the refractory phase on both arc erosion and contact resistance makes it possible to properly select a composite to be used for contacts in electric switches. Developed and tested contact materials Ag-W75, Ag-W50 and Ag-WC-C may find application in low-voltage switches for rated currents higher than 100 A. Composites Ag-WC can be used in compact switches as well as elements of alternating current contactors at the load of 250 A and voltage of 500 V. They are likely to replace Ag-CdO contact materials, which are currently withdrawn due to their toxicity. Especially the Ag-WC60 and Ag-WC70 composites can be used in extinguishing contacts of low-voltage switches. Last but not least, thanks to their high tacking resistance, Ag-WC60 contacts are suitable for medium- and high-voltage contacts, substituting for Cu-W contacts with a very low tacking resistance.

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