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INFLUENCE OF CHEMICAL COMPOSITION AND PRODUCTION PROCESS PARAMETERS ON THE STRUCTURE AND PROPERTIES OF SILVER BASED COMPOSITES WITH ZnO

OCENA WPŁYWU SKŁADU CHEMICZNEGO ORAZ PARAMETRÓW WYTWARZANIA NA STRUKTURĘ I WŁAŚCIWOŚCI KOMPOZYTÓW NA OSNOWIE SREBRA Z UDZIAŁEM ZnO

The paper shows results of the study into influence of chemical composition and consolidation process conditions on changes of physical and electrical properties of silver-based composites used in production of electric contacts. The investigations addressed influence of content of zinc oxide (ZnO) and modifying additions in a form of silver tungstate (Ag_2WO_4) and silver molybdate (Ag_2MoO_4) on changes in density, porosity and electrical conductivity. Density of the produced compacts was established by geometric method. The results of density measurements were used in determination of total porosity of sinters. Also arc erosion was examined to determine applicability of the produced composites for production of electric contacts. The erosion was measured as mass loss of individual materials after specific number of connections. The studies were conducted at current intensity of 10 A and voltage of 500V. The scope of the studies covered also evaluation of kinetics of sintering of the examined composites and determination of the mechanisms of mass transport in the process. Studies into kinetics of sintering were conducted in the air atmosphere at constant temperature of 900°C.

Production of the examined composite materials consisted of mechanical synthesis of powders of silver, zinc oxide and silver tungstate and molybdate, and then their consolidation by two-sided pressing and subsequent sintering. In cold pressing various pressures were applied 200, 300 and 400 MPa. Sintering was performed with a partial participation of liquid phase in temperature of 900°C. Also additional two-sided pressing was applied under pressure of 500 MPa and stress-relieving recrystallization annealing was performed as the final operation.

Keywords: Contact materials, compaction, sintering, physical properties, arc erosion

W pracy przedstawiono wyniki badań wpływu składu chemicznego oraz parametrów procesu konsolidacji na zmiany właściwości fizycznych oraz elektrycznych materiałów kompozytowych na osnowie srebra przeznaczonych na styki elektryczne. Analizie poddano wpływ zawartości tlenku cynku (ZnO) oraz dodatków modyfikujących w postaci wolframianu srebra (Ag_2WO_4) oraz molibdenianu srebra (Ag_2MoO_4) na zmiany gęstości, porowatości oraz przewodności elektrycznej. Gęstość uzyskanych wyprasek wyznaczono metodą geometryczną. Na podstawie uzyskanych wyników gęstości wyznaczono porowatość całkowitą spieków. Wykonano również badania erozji łukowej jako parametru określającego przydatność wytworzonych materiałów kompozytowych do zastosowania na styki elektryczne. Miarą erozji był ubytek masy poszczególnych materiałów po określonej liczbie łączeń. Badania zostały przeprowadzone przy natężeniu 10 A i napięciu 500 V. W ramach badań dokonano również oceny kinetyki spiekania badanych materiałów kompozytowych oraz podjęto próbę określenia mechanizmów transportu masy jakie występują podczas tego procesu. Badania kinetyki spiekania prowadzono w atmosferze powietrza w stałej temperaturze wynoszącej 900°C.

Proces wytwarzania badanych materiałów kompozytowych obejmował mechaniczną syntezę proszków srebra, tlenku cynku oraz wolframianu i molibdenianu srebra, a następnie ich konsolidację poprzez dwustronne prasowanie i następujące po nim spiekanie. Zabieg prasowania prowadzono na zimno, stosując różne ciśnienie prasowania 200, 300 oraz 400 MPa. Proces spiekania przebiegał z częściowym udziałem fazy ciekłej w temperaturze 900°C. Zastosowano także dodatkowe prasowanie dwustronne pod ciśnieniem 500 MPa oraz jako zabieg końcowy wyżarzanie rekrystalizująco-odprężające.

1. Introduction

New possibilities for control of properties of sinters by proper selection of process conditions and progress in development of electrical engineering spurred development of materials of controlled electrical and thermal conductivity. The constantly growing requirements

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on transfer of higher amount of electrical energy and reduction of its loss stimulates search for new contact materials [1÷3].

Silver based composites with addition of metal oxides, carbides and nitrides represent a large group of contact materials. Beside basic oxides (CdO, SnO_2, Fe_2O_3) the contact materials may contain also small amounts of additives in a form of Bi_2O_3, In_2O_3, WO_3, Ag_2WO_4. Contact materials are also made from metal alloys which contain two or three components. The most widely used are alloys of such systems as Ag-Cu, Ag-Ni, Ag-Cd, Ag-W, Cu-Be, Cu-W, Cu-Mo. Majority of the materials is produced by powder metallurgy methods, by mixing and milling of powder components or by application of internal oxidation. There are, however, technological problems of non-uniform mixing of powder components which results in heterogeneous structure and, in consequence, in decrease of mechanical and electrical properties. It can be especially observed in the composites of ultrafine structure with large content of hardening phase. The powder metallurgy methods consists of operations of compaction and then sintering or combination of both processes with application of subsequent process of secondary compaction or extrusion [3÷8].

Conditions of contact operation set specific requirements, and the most important are: the highest possible electrical and thermal conductivity, low tendency to transport material from one pole to the other, high arc resistance and capacity for arc suppression. The final properties of contacts and contact materials depend mostly on their microstructure, especially on the degree of oxide phase dispersion. Decrease of the size of particles of oxide phase improves erosive properties of the material in the same way as the decrease of porosity [6, 9, 10].

The study presented in this paper focused on new contact materials of Ag/ZnO type, which can be seen as a potential substitute for widely used and harmful cadmium containg Ag/CdO materials. The objective of the investigations was to determine influence of chemical composition and process conditions on structure and properties of silver based composite materials with oxide phase (ZnO) produced by powder metallurgy methods.

2. Experimental

In the studies Ag and ZnO powder made by Chempur company was used as initial material. Ag powder was produced by atomisation of liquid metal with water stream of properly selected pressure in experimental installation. High purity (99.99%) Ag_2WO_4 and Ag_2MoO_4 made by Sigma-Aldrich were used as modifiers.

Depending on the amount of modifiers (Ag_2WO_4, Ag_2MoO_4) the content of hardening phase (ZnO) was from 7.65 to 11.75 wt %. Average grain size of Ag, ZnO, Ag_2WO_4 and Ag_2MoO_4 powder was: 27.6, 2.4, 1.84 and 7.6 μm, respectively. The shape of silver powder particles was close to spherical and they had relatively smooth surface while zinc oxide was in a form of agglomerates composed of strongly packed particles in polyhedron shape.

The prepared powders were mixed and milled in a planetary Retsch PM 400 ball mill. The following conditions were applied during milling: rotational speed 200 rev/min, 60 minutes operation / 30 seconds break. Steel milling bodies and containers were used in milling. Ball diameter was about 10 mm, and the ball to powder mass ratio was 4:1. To increase milling process efficiency a wetting agent in a form of acetone was applied. Milling was conducted in the air in room temperature. Milling time was 10 hours.

The mixtures of Ag/ZnO, Ag/ZnO+Ag_2WO_4 and Ag/ZnO+Ag_2MoO_4 powders were compacted. Two-sided cold compaction was applied with various pressures: 200, 300 and 400 MPa. In the result of compaction operation cylindrical samples of dimensions Ø10×5 and 10×15 mm were produced. Stress relief reducing annealing was applied (300°C/1h/air) before compaction. Sintering was conducted with liquid phase in temperature of 900°C, in the air atmosphere. Additional compaction with pressure of 500 MPa was applied to reduce material porosity. The final operation consisted of recrystallization stress relief annealing in temperature of 800°C.

In the produced powder mixtures density and specific surface were measured by adsorption of gas molecules (BET) method with Gemini 2360 equipment. Density of compacts was determined by geometrical method based on dimensions of the samples. The produced density results were used for determination of total porosity of the samples. There were also studies performed into kinetics of sintering of the examined composite materials. In order to do that cylindrical samples were formed of dimensions 10×5 mm by compaction method involving uniaxial pressure of 200 MPa. Sintering kinetics was examined in the air and in constant temperature of 900°C. The sample was placed in a measuring system and changes of linear dimensions of the diameter were measured within an accuracy of ±0.001 mm. Temperature was measured with thermocouple of K type within an accuracy of 1°C.

Electrical conductivity was measured with eddy-current SIGMATEST 2.069 instrument. Microstructure of the examined composite materials was characterised by ligh microscope Olympus GX71F.

Results of examination of electric arc erosion were used in determination of electrical and functional properties of the composites. Mass loss of individual samples after certain number of switching operations in the range of 0-50 thousand was a measurement of the erosion. Arc erosion tests were performed under model conditions in a computer controlled test system. A control-measuring MPK module was used as an interface between the computer and test instrument to register changes of voltage and current with time. The following mechanical parameters were applied in measurements: contact gap – 6 mm, contact tilt 2 mm, contact force 15 N, retracting force 20 N, while the electrical parameters were as follows: test current 10 A, voltage 500 V, arc duration 10 ms, switching frequency 25/min, number of switching operations 50.000.

3. Results and discussion

The produced powder mixtures Ag+ZnO, Ag+ZnO/Ag_2WO_4 and Ag+ZnO/Ag_2MoO_4 were examined and their density and specific surface were measured. The results are presented in Table 1. The mixture which contains ZnO only shows the highest specific surface at the level of 1.26 m^2g^{-1}, while the lowest (0.56 m^2g^{-1}) was observed in the mixture which contains about 7.65-7.75 wt % of ZnO with addition of silver molybdate (Ag_2MoO_4). Small addition of a modifier in a form of Ag_2MoO_4 brings increase of bulk density of the whole powder mixture. The produced powder mixtures have grains of micrometric structure and size within the range 5.7–16.1 μm. The smallest grain of size 5.7 μm was observed in the mixture of composition Ag+11.75ZnO+0.25Ag_2MoO_4.

Kinetics of sintering of the examined composite materials was determined from the registered curves of linear contraction changes as a function of time (Fig. 1), which then, by finding their logarithms, were transferred into a linear form (Fig. 2, 3). It made possible to distinguish sections of various slopes of a straight line. Following the model sintering description according to Kuczynski [11÷14] the value of exponent m was used to determine prevailing mechanisms of mass transport in individual stages of sintering. The exponent m in the first stage of sintering of all examined composite materials shows that compaction process is controlled by grain rearrangement. The values of exponent m are greater than unity which leads to a conclusion that the process takes place with presence of liquid phase. The first stage of sintering takes several minutes and is very intensive. The second runs slowly and lasts for several hours. The determined in the second stage of sintering values of exponent m imply that the compaction takes place in the result of dissolving-crystallization process. In the composites with silver molybdate (Ag_2MoO_4) addition the exponent value is close to 0.5 which implies that the process is controlled by rate of solid phase dissolution in the liquid. In the composites which contain only oxide phase (ZnO) or small addition of silver tungstate the exponent value is at the level of 0.3. In those materials the dissolving-crystallization process is probably controlled by rate of diffusion in liquid phase. Theoretical value of m exponent in that process is 1/3. The differences in behaviour during sintering of materials with different chemical composition can already be observed on the curves of linear contraction changes as a function of time (Fig. 1). The samples made of composites with silver molybdate show smaller contraction and gentler sintering process when compared to the composites with silver tungstate (Fig. 1).

TABLE 1

Properties of the powder mixture

Composition of powder mixture, wt. %.	**Bulk density, g/cm^3**	**Flow rate of powder, s/50g**	**Density, g/cm^3**	**Specific surface, m^2g^{-1}**	**Average grain size, μm**
Ag + 8ZnO	2,43	no	9,78	1,26	13,3
Ag + 7,75ZnO + 0,25Ag_2WO_4	2,62		9,97	0,98	14
Ag + 7,75ZnO + 0,35Ag_2WO_4	2,6		9,94	1,13	14,9
Ag + 7,75ZnO + 0,25Ag_2MoO_4	2,89		9,75	0,56	16
Ag + 7,65ZnO + 0,35Ag_2MoO_4	2,43		9,74	0,57	16,1
Ag + 9,75ZnO + 0,25Ag_2WO_4	2,13		9,56	0,68	7,9
Ag + 9,75ZnO + 0,25Ag_2MoO_4	2,91		9,56	0,79	9,7
Ag + 11,75ZnO + 0,25Ag_2WO_4	2,86		9,44	0,77	7,6
Ag + 11,75ZnO + 0,25Ag_2MoO_4	2,91		9,43	0,88	5,7

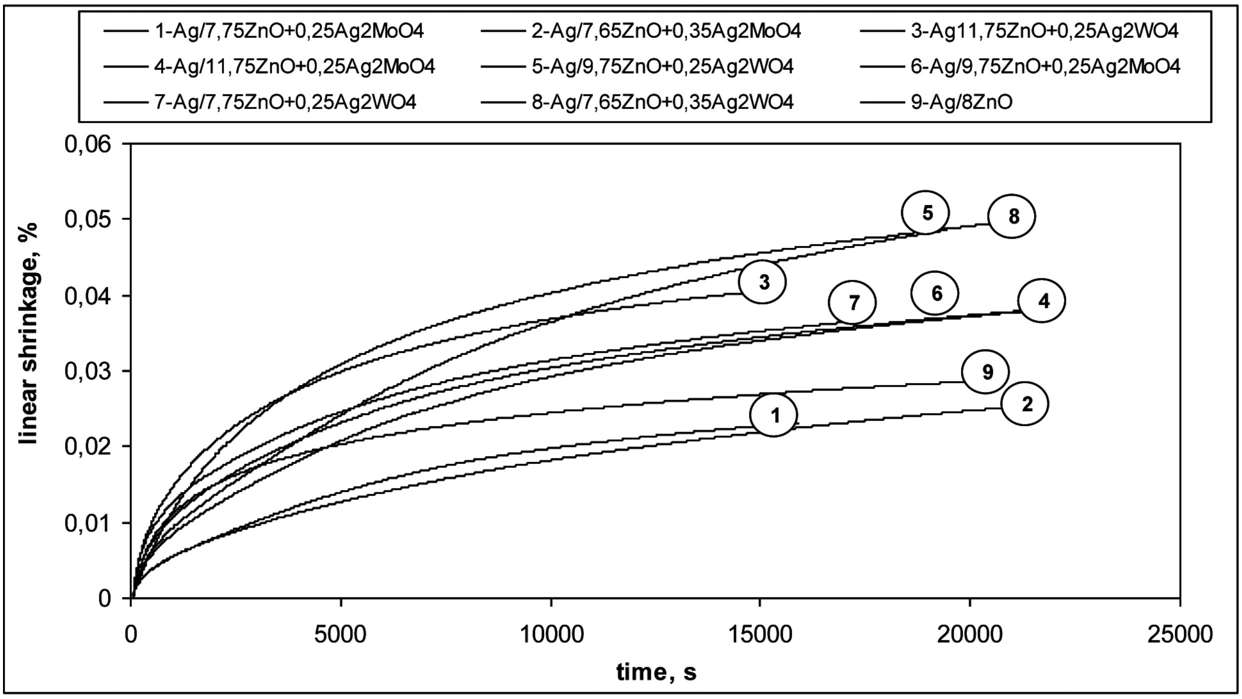

Fig. 1. Linear shrinkage curves as a function of time for the examined composites

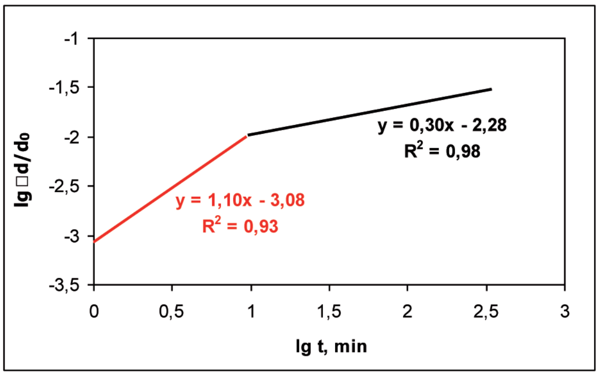

Fig. 2. $\Delta L/L_0$ = f(t) curves showed in the logarithmic coordinates for the Kuczyński model of Ag/8ZnO composites

Application of the examined composites in electrical contacts is determined by production of relatively homogenous material of compact structure and high density. Changes in physical density and porosity of compacts were used as criteria for evaluation of efficiency of compaction and sintering. The presented relations (Fig. 4) show that regardless of the applied pressure of compaction the highest density is observed in the composites of the lowest zinc oxide content and with addition of 0.25 wt% of Ag_2WO_4. With the increase of oxide phase content gradual decrease of density is observed. Addition of modifiers in a form of silver tungstate (Ag_2WO_4) and molybdate (Ag_2MoO_4) does not change that parameter significantly, while their influence on density changes is comparable. There is, however, a strong influence of pressure of compaction. The pressure increase results in density increase, and the largest differences can be observed in the range 200-300 MPa. The pressure increase to 400 MPa brings further but small increase of density of the produced sinters. With the change of density of compacts also change in their porosity is observed (Fig. 5). The lowest porosity was reached when high pressure (400 MPa) was applied. The presented results of total porosity examination show the lowest porosity in the composites with addition of ZnO exclusively. In such composites the porosity reaches 5%. Increase of oxide phase content leads to increase of compact porosity degree. From among the sinters compacted with pressure of 400 MPa the lowest porosity at the level of 10% was reached in the Ag/11.75ZnO+0,25Ag_2WO_4 composites (Fig. 5).

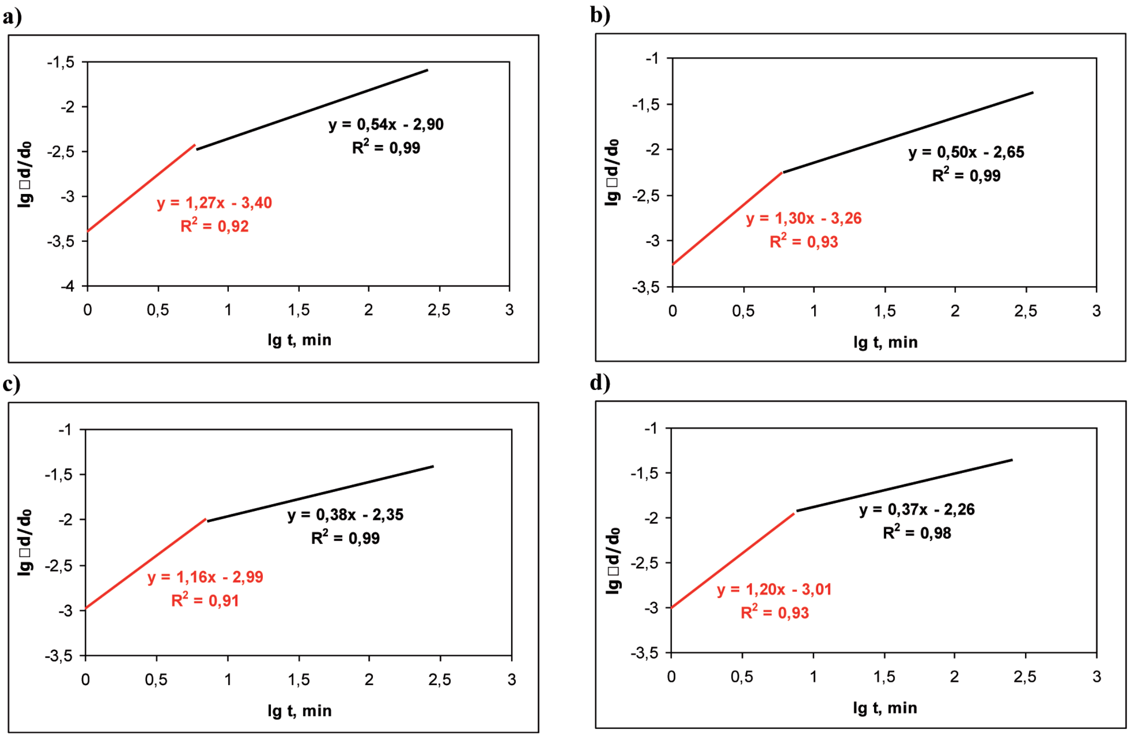

Fig. 3. $\Delta L/L_0$ = f(t) curves showed in the logarithmic coordinates for the Kuczyński model of composites: Ag/7,75ZnO+0,25Ag_2MoO_4 (a), Ag/11,75ZnO+0,25Ag_2MoO_4 (b), Ag/7,75ZnO+0,25Ag_2WO_4 (c), Ag/11,75ZnO+0,25Ag_2WO_4 (d)

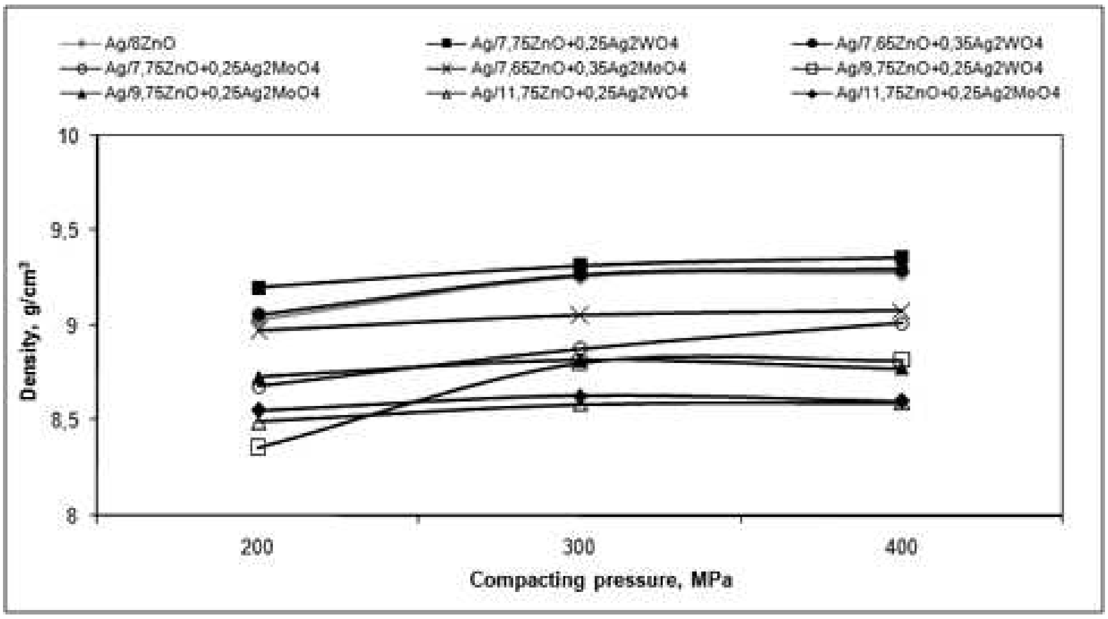

Fig. 4. Compressibility curves of examined composites

Results of electrical conductivity examinations (Fig. 6) indicate large changes of electrical conductivity of the examined materials with their chemical composition. The highest conductivity at the level of 46 MS/m is observed in the composites with a small oxide phase (ZnO) content (7,65 wt %), which additionally contain 0.25 wt % of Ag_2WO_4. Despite the fact that electrical conductivity of silver is higher by several orders of magnitude than oxide phase particles, their presence significantly worsens electrical properties of the whole composite. The decrease of electrical conductivity of the composite is also influenced by volume fraction of the matrix and particles of oxide phase as well as by difference in their electrical resistivity. That is why in the composites of high (11.75 wt %.) ZnO content lower conductivity is observed than in the materials of lower content of that phase. Beside chemical composition also the applied pressure has influence on the changes in conductivity. In all the examined composite materials a regularity of conductivity increase with pressure increase is observed which results from the decrease of porosity. It has a negative influence on electrical properties of the whole composite material.

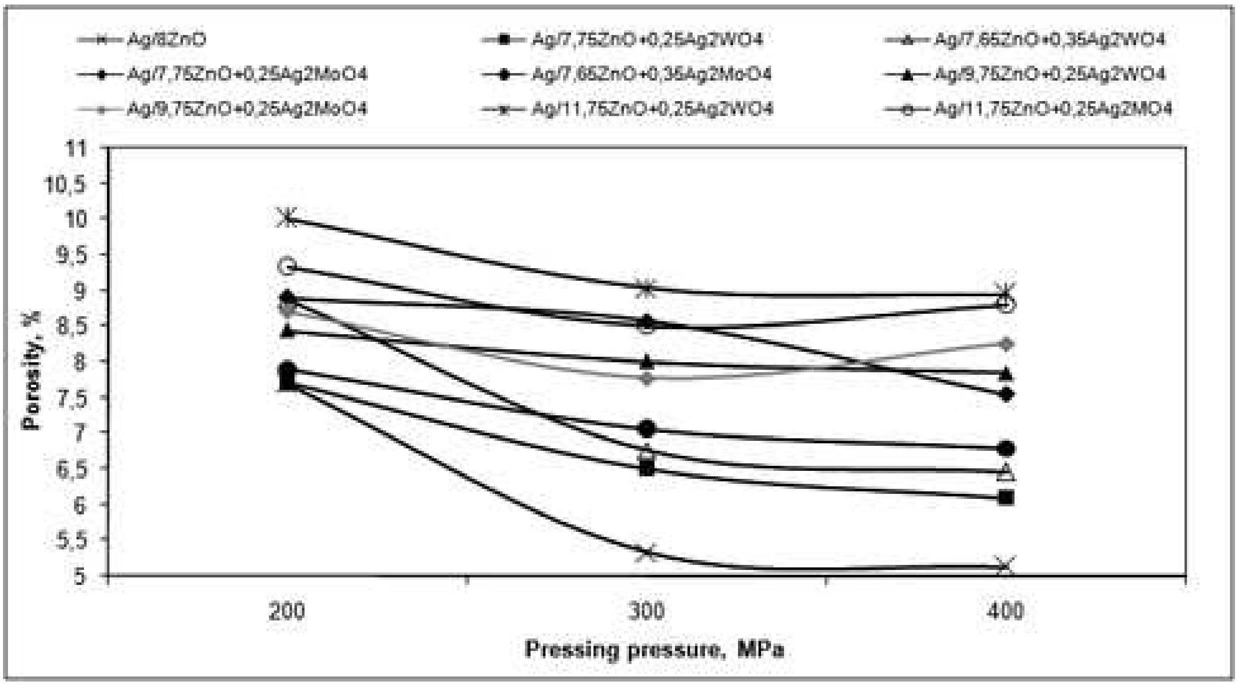

Fig. 5. Changes in total porosity of composites with diverse chemical composition vs. applied compaction pressure

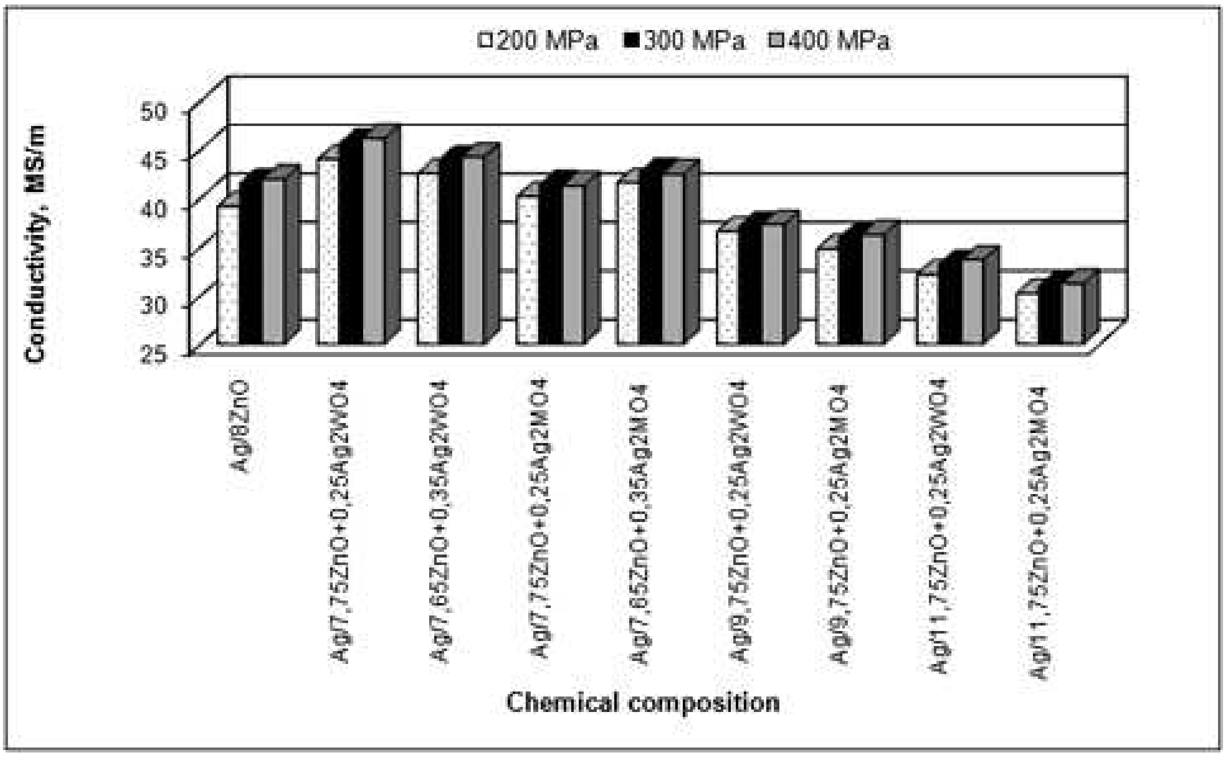

Fig. 6. Effect of chemical composition and compaction of metal powders on electrical conductivity

Microstructure observations of examined composite materials were made on etched microsections, both longitudinal and transverse to the compacting direction. Figures 7-9 show microstructure of composites of various chemical composition produced by compaction under the pressure of 400 MPa. It was found that the produced composite materials characterized relatively compact and homogenous structure. They also reveal high degree of sintering. The performed analysis of microstructure of the examined materials demonstrated that distribution of oxide phase particles in the matrix is not uniform. It is located mainly at the borders of strongly elongated silver grains. The structure is of band character and shows traces of plastic deformation (Fig. 7-8b). The observed effects of strong structure deformation result from previously performed hardening of the material. Silver matrix grains have irregular shape and diversified size with visible recrystallization twins (Fig. 7, 8b, 9a). The observed changes and structural effects are the outcome of hardening operation and processes of polygonization and static recrystallization which take place during the final annealing in the previously deformed material.

The studies into arc erosion were performed to assess applicability of the composite materials for contact products. The reactions of oxidation and reduction which take place on the contact surface bring changes to the material surface properties (conductivity) and to the resistance of electrodes, and results in decrease of the contact surface layer resistance to thermal shocks. That is why the contact materials should display strong resistance to changes of those parameters.

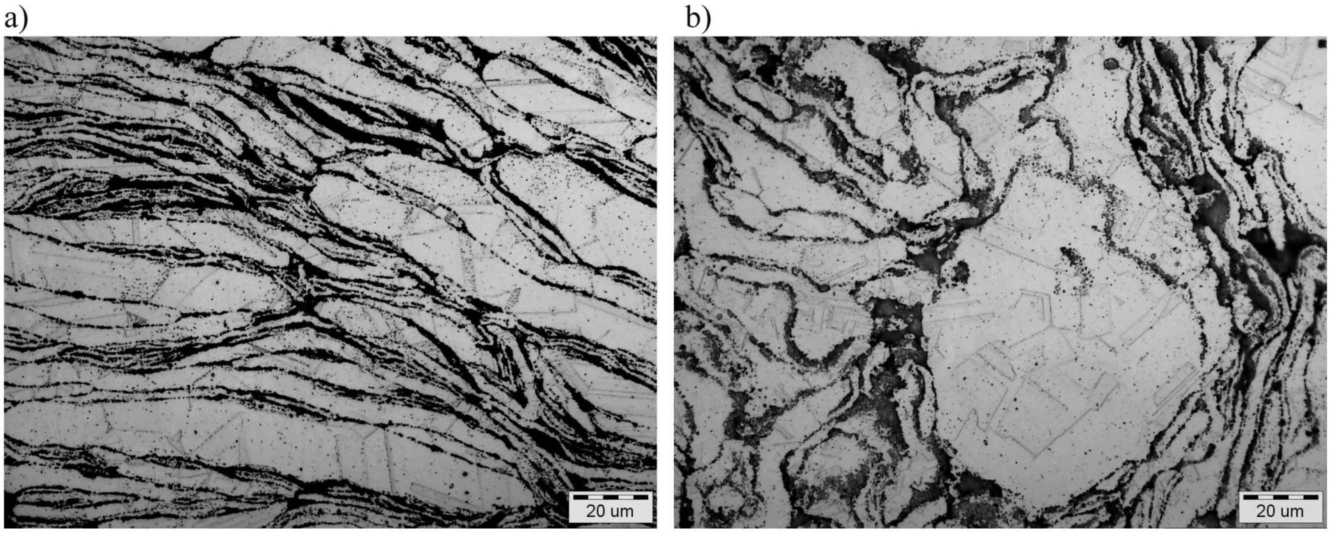

Fig. 7. Microstructure of composite Ag/8ZnO compacted with pressure 400 MPa: longitudinal (a), crosswise (b) microsection

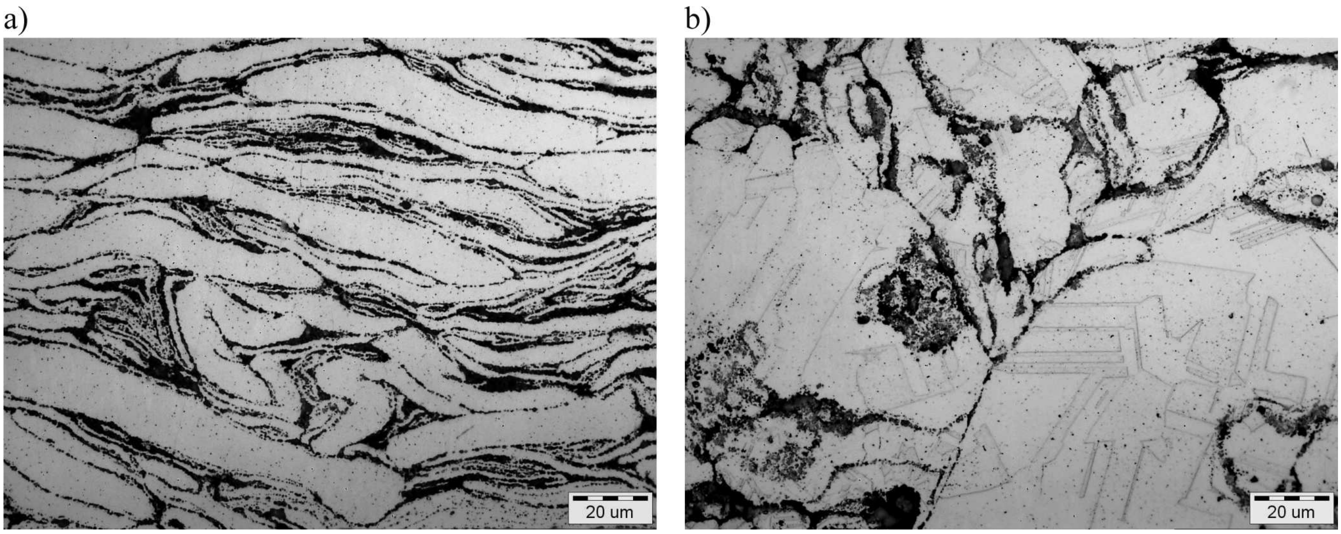

Fig. 8. Microstructure of composite Ag/ZnO+Ag_2WO_4 compacted with pressure 400 MPa: longitudinal (a), crosswise (b) microsection

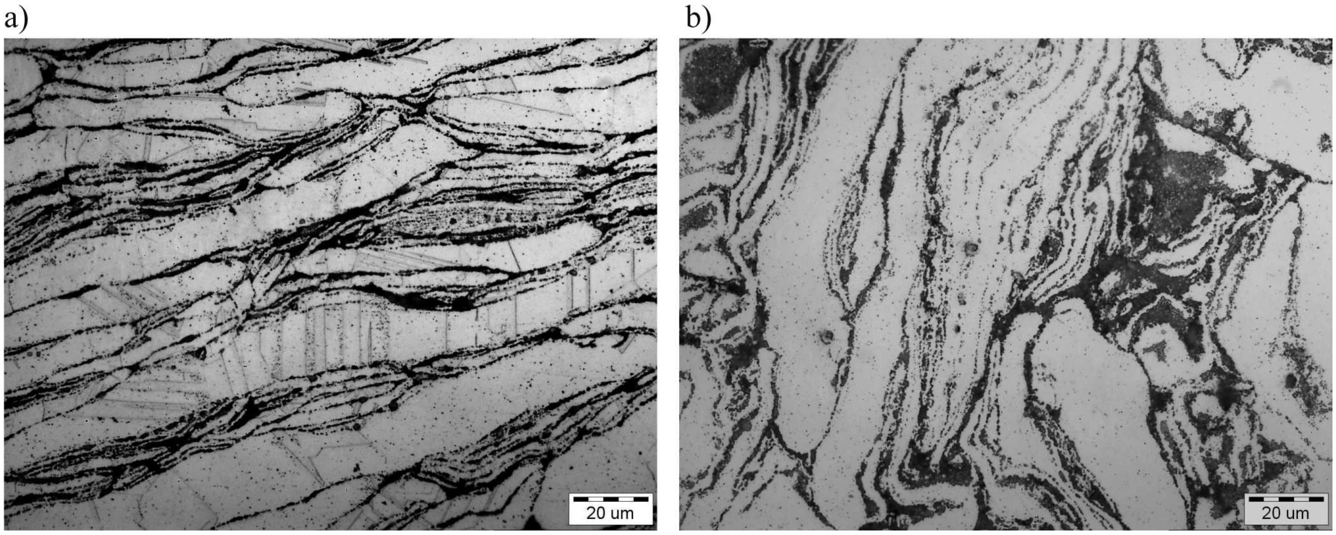

Fig. 9. Microstructure of composite Ag/ZnO+Ag_2MoO_4 compacted with pressure 400 MPa: longitudinal (a), crosswise (b) microsection

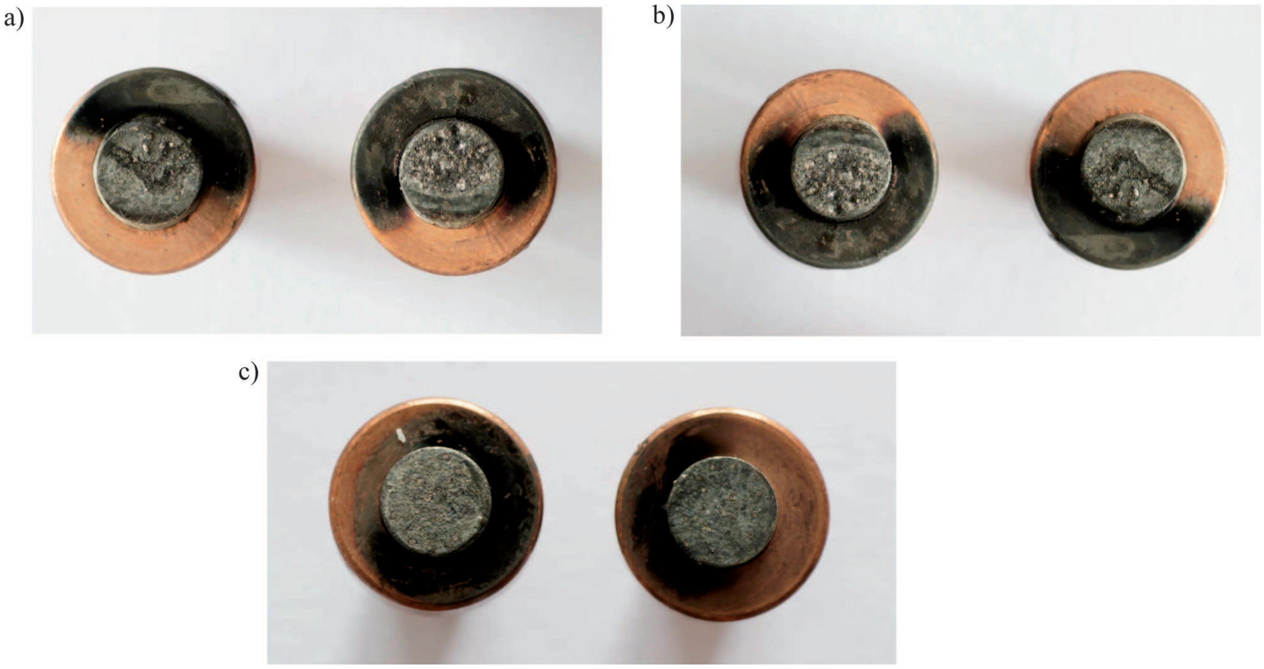

Fig. 10. Surface of contacts of composites Ag/8ZnO (a), Ag/9,75ZnO+0,25Ag_2MoO_4 (b) Ag/9,75ZnO+0,25Ag_2WO_4 (c) after electric arc operation

Surfaces of contacts made of selected composite materials after electric arc operation are presented in Figure 10. The analysis of contact surface after 50,000 switching operations indicate that the contacts made of Ag/8ZnO and of Ag/11.75ZnO+0.25Ag_2WO_4 show local silver evaporation combined with eruption of drops from surface layer (Fig. 10 a, b). Also a tendency for formation of craters and spongy areas in the composite structure was noticeable which results from the phenomenon of material transfer from anode to cathode as confirmed by the changes of mass loss presented in Fig. 13. Transfer of material during arc operation results from transport of gaseous and liquid particles. No traces of structure degeneration were observed on the surface of the contacts made of other composite materials (Fig. 10c), only thin layer generated during surface oxidation was visible. Figures 11 and 12 present examples of diagrams of dependency between the contact mass loss Δm and the number N of switching cycles. Transport of silver from anode to cathode dominates in the contacts produced from Ag/9.75ZnO+0.25Ag_2MoO_4 composite (Fig. 11). Such a phenomenon is not observed in Ag/9.75ZnO+0.25Ag_2WO_4 composite materials (Fig. 12). In the first 20,000 cycles the mass increase in both electrodes was at comparable level. With the further increase of the number of switching operations the erosion resistance of the materials changes, which can be explained by generation of different amounts of oxides. Figure 13 shows comparison of maximum mass loss in the contacts produced from the examined composite materials. Based on the analysis of those relations it can be established that the mass loss of contacts significantly decreases with the silver content increase above 90 wt %. Melting and spattering of melted metal is generated by moving electric arc during operation of contacts. Presence of ZnO particles and additives in a form of Ag_2WO_4 and Ag_2MoO_4 increases silver viscosity which results in lower loss from spattering. The conducted tests demonstrated that all the examined materials show high erosion resistance, however the best erosion properties were observed in the composites which contain 7.75 and 9.75 wt % of ZnO and addition of Ag_2WO_4 and Ag_2MoO_4 in the amount of 0.25 wt %. The examined composites show no tendency to locking and low tendency to material transfer between the contacts.

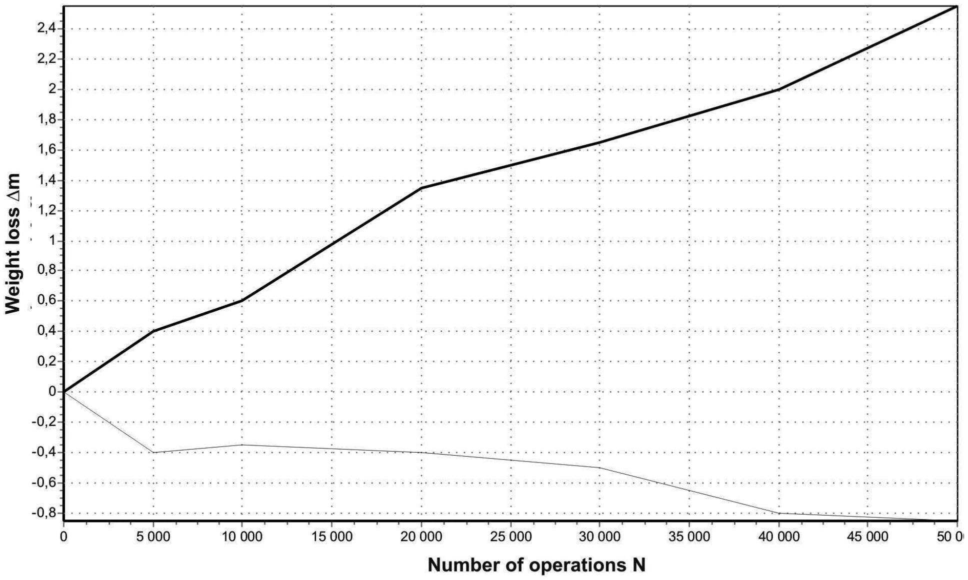

Fig. 11. Relation between contact mass loss and number of switching operations of composites Ag/9,75ZnO+0,25Ag_2MoO_4

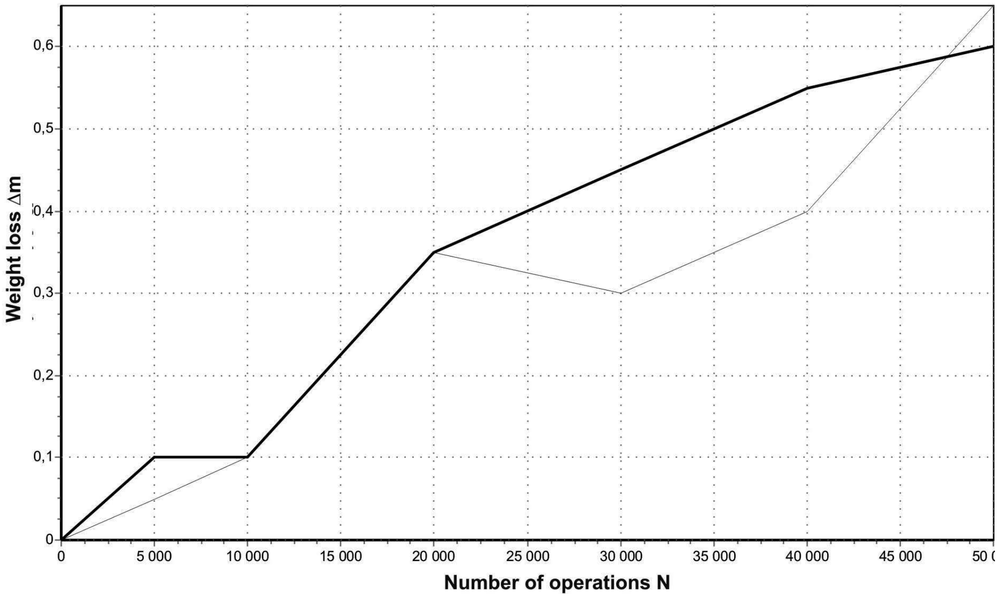

Fig. 12. Relation between contact mass loss and number of switching operations of composites Ag/9,75ZnO+0,25Ag_2WO_4

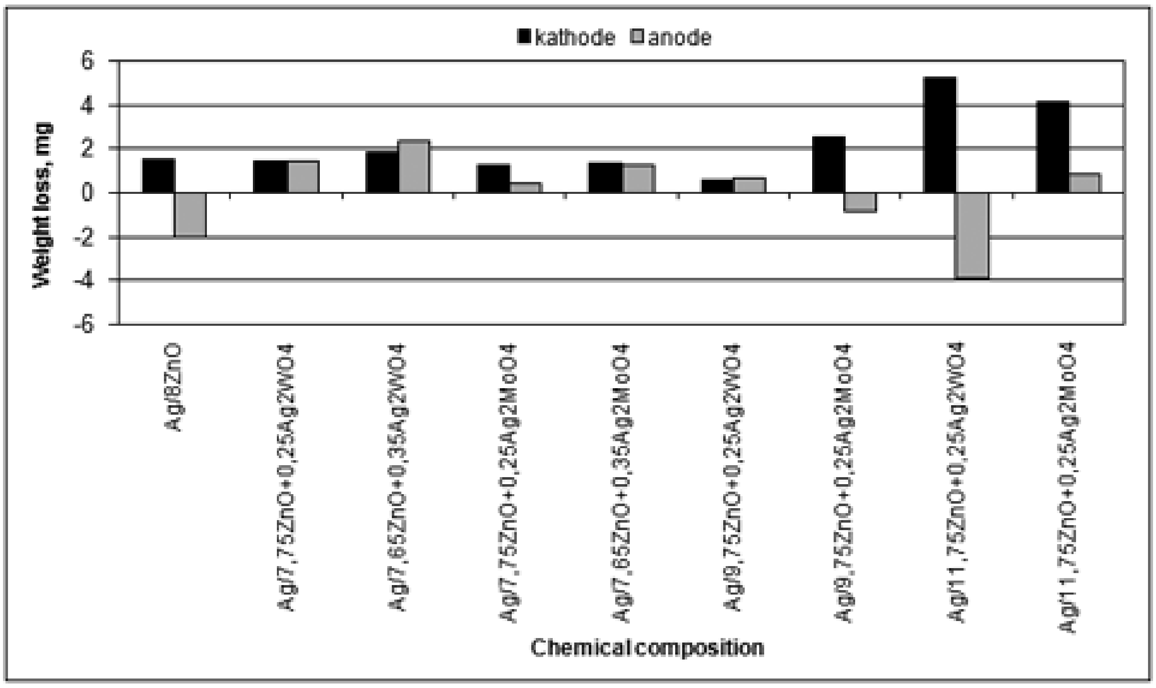

Fig. 13. Erosion degree of examined composite materials

4. Conclusions

1. On the base of studies of kinetics of sintering it was established that in the first stage the process of compaction in all the examined composites is controlled by grain rearrangement and takes place in presence of liquid phase. In the second stage the compaction results from dissolving-crystallization process. In the case of composites with silver molybdate (Ag_2MoO_4) the process is probably controlled by the rate of solid phase dissolution in the liquid. In the composites containing oxide phase (ZnO) only and with some small addition of silver tungstate (Ag_2WO_4) the dissolving-crystallization process is controlled by the rate of diffusion in liquid phase.
2. Addition of small (0.25 wt %) amount of a modifier in a form of silver tungstate (Ag_2WO_4) results in increase of electrical conductivity of the whole composite material.
3. To produce homogenous material of high density and good physical properties it is recommended to use the highest possible pressure.
4. Distribution of particles of oxide phase in the matrix is not uniform; the phase is located mainly at the borders of deformed silver grains. In the microstructure of the examined composites effects related to the processes of strain hardening and structure restoration are observed.
5. The produced composite materials show high arc resistance. Presence of small amounts of modifiers in a form of silver tungstate or molybdate increases erosion resistance of the examined materials.
6. The analysis of the produced results shows that the best erosion properties were observed in the composite materials which contain 7.75 and 9.75 wt % of ZnO and addition of Ag_2WO_4 and Ag_2MoO_4. In other examined composites a small phenomenon of material transfer by plasma stream from one pole to the other was observed.

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