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FABRICATION AND PROPERTIES OF SILVER BASED MULTIWALL CARBON NANOTUBE COMPOSITE PREPARED BY SPARK PLASMA SINTERING METHOD

WYTWARZANIE I WŁAŚCIWOŚCI KOMPOZYTU NA BAZIE SREBRA Z DODATKIEM NANORUREK WĘGLOWYCH OTRZYMANEGO METODĄ SPS

The paper presents results of investigations of the obtained nanocomposite materials based on silver with addition of multiwall carbon nanotubes. The powder of carbon nanotubes content from 0.1 to 3 wt. % was produced by application of powder metallurgy methods, through mixing and high-energetic milling, and also chemical methods. Modification of carbon nanotubes included electroless deposition of silver particles on the carbon nanotube active surfaces and chemical reduction with strong reducing agent – sodium borohydride ($NaBH_4$). The obtained powder mixtures were consolidated by SPS – Spark Plasma Sintering method. The formed composites were subjected to tests of relative density, electrical conductivity and electro-erosion properties. Detailed examinations of the structure with application of X-ray microanalysis, with consideration of carbon nanotubes distribution, were also carried out. The effect of manufacturing methods on properties of the obtained composites was observed.

Keywords: Spark Plasma Sintering, Composites, Ag - Carbon Nanotubes, Dispersion, Microstructure

1. Introduction

The dynamic technological development observed in recent years is a driving force for development of the new materials. The role of composite materials, including nanomaterials, is particularly important as it is one of the most promising and the fastest growing group of materials. It covers, among others, materials with metallic, cermetallic or polymer matrix with addition of carbon nanotubes (CNTs). Properties of these materials can significantly differ from materials of the same chemical and phase compositions but consisting of larger structural elements. Furthermore, large surface development increases chemical reactivity while high content of defects has impact on magnetic, electrical and optical properties of the material, which results in the change of properties [1].

Additionally, what is especially relevant in the case of composite materials, specific structure of the nanomaterials causes qualitatively different material reactions to external factors, e.g. specific mechanism of plastic deformation. It can result in increase of creep strength, resistance to thermal fatigue or abrasive wear [2].

Carbon nanotubes are allotropic forms of carbon and are characterized by several advantageous properties: high mechanical strength and stiffness, good electrical and thermal conductivity (for SWCNT: 1800-6000 W/mK) and wear resistance. The other relevant parameter is their low coefficient of thermal expansion (CTE~0) enabling application of carbon nanotubes in the metal matrix wherever high thermal stability is required [3].

Tensile strength of carbon nanotubes is about 50 times higher than corresponding figure for steel. Carbon nanotubes are characterized by low density (ρSWCNTs=0,6 g/cm^3, ρMWCNTs=1-2 g/cm^3), what has an essential effect on the mass reduction of the whole composite without deterioration in its mechanical properties. Homogeneous distribution of carbon nanotubes in the metal matrix is the major requirement for production of composites of demanded physicochemical properties. There are publications, which describe procedures for modification of carbon nanotubes in order to obtain required powder mixtures. Some of the methods mention the decorating of nanotubes with such metals as: Ni, Pd, Au, Ag [4, 5, 6]. Silver is of particular importance because of its high electrical and thermal conductivity when compared to the other metals. Since there is no wetting of carbon nanotubes with silver, methods for production of such composites include chemical vapour deposition [13], electroless deposition of metal particles on the carbon nanotubes surfaces and chemical reduction. The nanotubes, which are obtained as a result of synthesis, are strongly agglomerated and spliced, while

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Van der Waals forces between carbon atoms and large specific surface make them difficult to be separated. That effect create important problems during production of composite materials of homogeneous dispersion [7].

2. Research and technological methods

Silver powder with purity level above 99.9% and grain size below 63 μm, and multiwalled carbon nanotubes in a form of powder from Haydale Company were used as the initial materials (Fig. 1). Table 1 presents physical properties of the powders.

TABLE 1
Physical properties of silver and carbon nanotubes powders

Powder	Density, g/cm^3	Specific surface, m^2/g	Bulk density, g/cm^3
Silver	10.33	0.17	1.47
Carbon nanotubes	2.06 (true density)	213.17	0.14

Large differences in density (Table 1) and lack of wettability of carbon nanoforms with silver bring problems of nanotubes homogeneous dispersion in metal. In order to resolve this problem a suitable method of preparation of silver-CNT powder material was applied. The mixtures were prepared by the following powder metallurgy methods: high-energy milling and chemical methods including electroless deposition.

The milling process was carried out in the Pulverisette 7 high-energy planetary ball mill by Fritsch in the containers made of tungsten carbide at the following process parameters: BPMR-ball to powder mass ratio – 4:1, time – 60 minutes, rotary speed – 800 rpm. The Ag – nC powder mixtures with addition of 3 wt% of multiwalled carbon nanotubes were produced.

The method for electroless deposition of silver particles on the surfaces of nanotubes included several processes. *Oxidation* by modified Hummers and Offeman method was the first stage, which consisted in addition of the concentrated sulphuric acid and successive addition of $KMnO_4$ to carbon nanotubes powder while maintaining the temperature at the level of about 20°C. Then temperature of mixture was increased to 35°C and kept at this level for 30 minutes. The slurry was diluted with H_2O, then its centrifugation was performed. *Sensitization* was the next operation, at this stage wet precipitate was combined with solution containing 0.1 M $SnCl_2$ and 0.1 M HCl. After that the *activation* of carbon nanotubes surfaces by addition of the solution containing 0.0014 M $PdCl_2$ and 0.25 M HCl to the wet precipitate was conducted. Then the slurry was subjected to rinsing and centrifuging for 20 minutes at 4600 rpm. S*ilver plating* of carbon nanotubes was the last stage carried out by reduction of 31.5 g of $AgNO_3$ in proportion to 2.0 g of CNTs. The produced powder contained 9.5wt% CNT. The formed in such a way material was used for preparation of powder mixtures with the following carbon nanotubes content: 1; 0.3; 0.1 wt% by mixing of Ag-9.5wt% CNT material with silver powder in the mixer for 20 hours.

In the first stage of the second method of chemical reduction, $AgNO_3$ was dissolved in distilled water, then carbon nanotubes were subjected to dispergation with ultrasounds in the prepared solution. Then reduction of silver ions by strong reducer of sodium tetrahydraborate ($NaBH_4$). After reduction process the precipitate was rinsed and dried in the drier for 4 hours at temperature of 120°C, the powder with 1wt% CNT was formed. As in the previous procedure the produced material was mixed with silver to obtain the final compositions with the following carbon nanotubes content: 1; 0.3 and 0.1 wt%.

The prepared powder mixtures were subjected to spark plasma sintering (SPS) with application of HP D5 equipment by FCT. The process was carried out in graphite mould in the vacuum at the following parameters: rate of heating – 100°C/min, sintering temperature – 700°C, pressure – 63 MPa, time – 3 minutes.

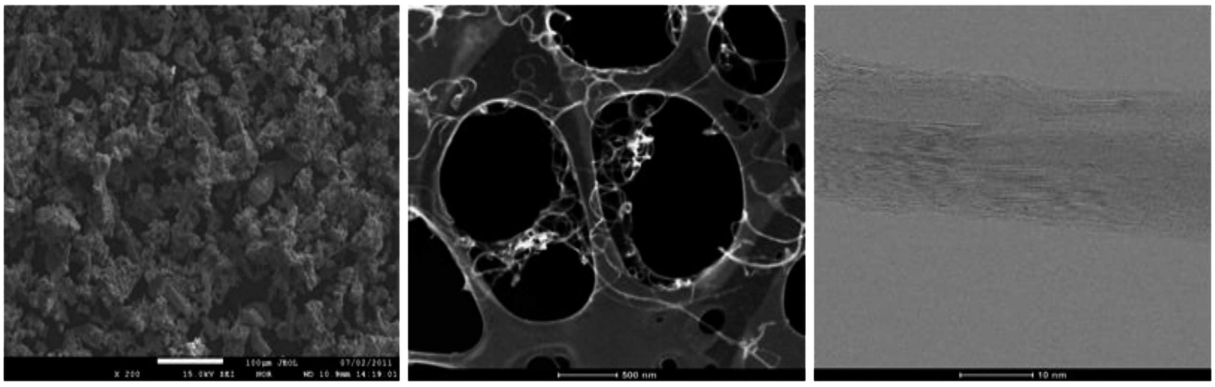


Fig. 1. Morphology of silver powder particles (magnification 200x) and multiwalled carbon nanotubes (image from transmission microscope)

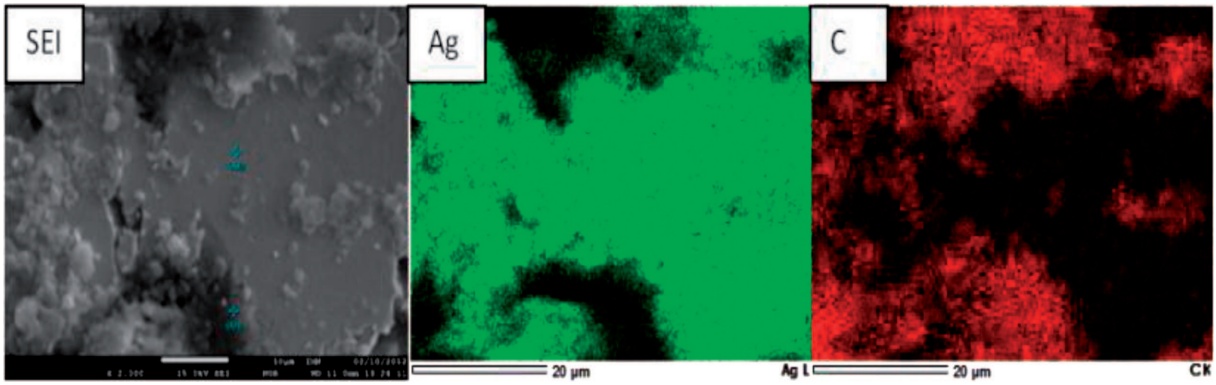


Fig. 2. Element distribution maps after 30 min. of high energetic milling. Magnification 2 000x

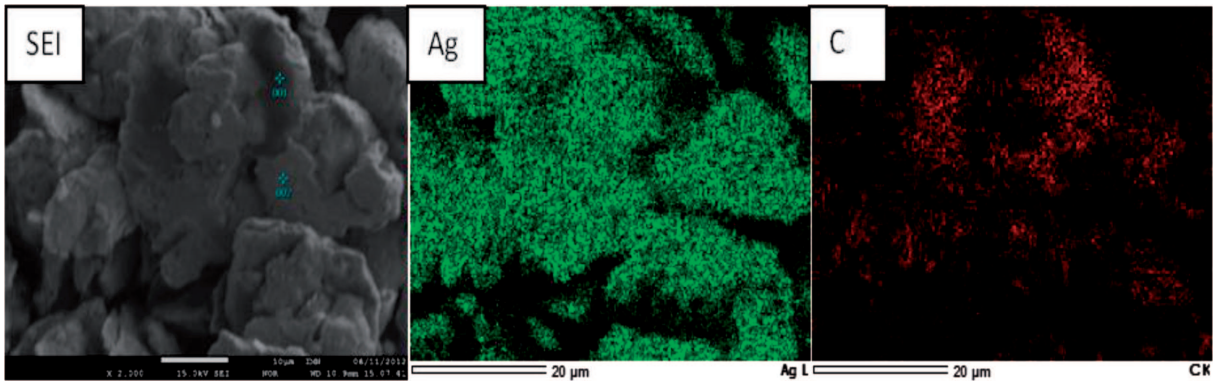


Fig. 3. Element distribution maps after 60 min. of high energetic milling. Magnification 2 000x

Density of the obtained materials was examined by pycnometer method with application of AccuPyc 1330 apparatus by Micromeritics. The electrical conductivity was tested by eddy current method on the Sigmatest 2.069 equipment by Foerster. The microstructure tests and chemical analysis in the microareas were performed with application of JXA 8230 X-ray microanalyser by Jeol. Electroerosion tests were conducted with application of testing equipment for examinations of arc erosion and contact resistance. Mass loss after subsequent switching tests was the basis of evaluation of the arc erosion resistance.

3. Research results and discussion

The powder of 3 wt% CNT was produced in high-energy milling operation. The powder with grains of flake-shaped morphology and unevenly distributed carbon forms on the silver particles surface was obtained as a result of the process carried out for 30 minutes (Fig. 2). Extension of process time to 60 minutes enabled better distribution of introduced carbon forms (Fig. 3). The time extension brings increase of specific surface from 7.69 m^2/g for 30 minutes of the milling to 8.89 m^2/g after 60 minutes, what indicates higher deformation of powder particles with increase of the milling time.

The morphology of powders prepared by chemical reduction and electroless deposition of silver particles on the carbon nanotubes surfaces is presented in Fig. 4.

As a result of chemical reduction of silver with strong reducer the powder with most of silver particles occurring in a form of agglomerates separately from carbon nanotubes was obtained.

Nanotubes completely or partially covered with silver particles can be observed in the microstructure. The powder produced by electroless deposition is characterized by more homogeneous distribution of silver particles between carbon nanotubes (Fig. 4). The powder was subjected to detailed chemical analysis. The analysis showed, besides silver and carbon, presence of tin powder in amount of 3.5 wt% and palladium – 0.43 wt%. These components are impurities formed after chemical processes. The other impurities of powder are: Cl, Mn, Ni, K (<0,01%) and oxygen at the level of 4.46 wt%.

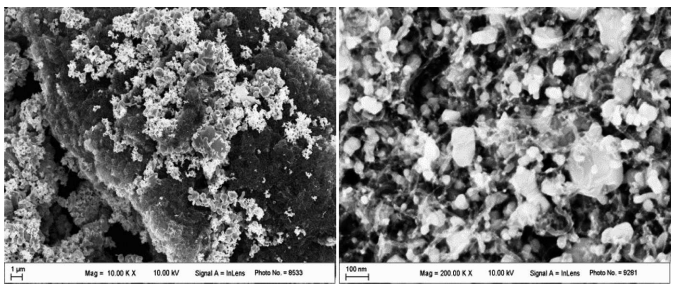


Fig. 4. SEM image of sample Ag-CNT after chemical reduction (left) and electroless deposition process (right)

As a result of the performed chemical operations Ag-CNT powder mixtures with nanotubes content at the level of 1wt% and 9.5wt% were obtained for powder after chemical reduction and the powder after electroless deposition, respectively.

Silver powder was added to the prepared mixtures in order to obtain composite of 0.1 and 0.3 wt% CNT.

Figures 5-7 present microstructure of the composites sintered by SPS method.

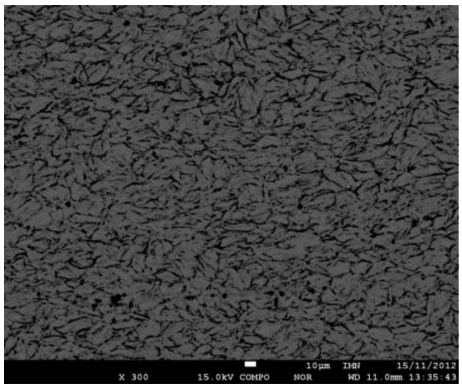


Fig. 5. Microstructure of sintered Ag-3wt%CNT composite. Magnification 300x

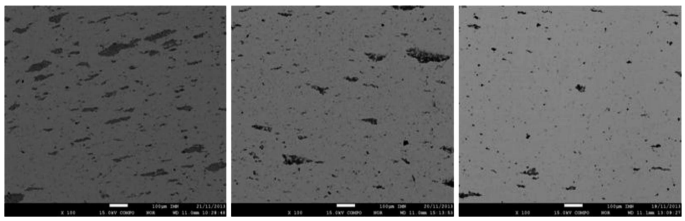


Fig. 6. Microstructure of sintered Ag-1wt%CNT composite (left picture), Ag-0.3wt%CNT (central picture), Ag-0.1wt% CNT (right picture) from the powder after electroless deposition. Magnification 100x

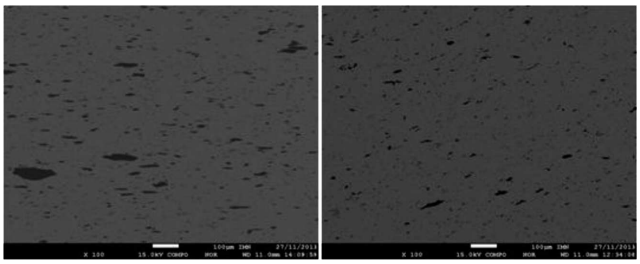
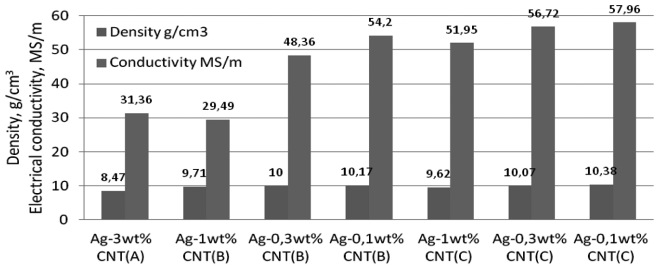


Fig. 7. Microstructure of sintered Ag-1wt%CNT composite (left picture), Ag-0.3wt%CNT (right picture) from the powder after chemical reduction. Magnification 100x

Bright areas of silver and dark areas of carbon nanotubes are visible in the microstructure of the produced sinters. In the sinter with 3wt% CNT significant volume fraction of nanotubes, despite their low addition, in relation to silver matrix is observed. Nanotubes are distributed homogeneously in the whole volume of the composite. The clusters of nanotubes in a form of bands and very small precipitates are visible in the composite obtained by preparation of powder with chemical methods. CNT-clusters are distributed homogeneously in the metal matrix. Microscopic observation shows that composites sintered by SPS method are characterized by low porosity.

Density of the produced materials (Fig. 8) is in the range from 8.47 for powder produced by high-energy milling (Ag-3wt%CNT(A)) to 10.38 g/cm^3 for powder prepared by chemical reduction (Ag-0,1wt%CNT(C)). The increase of content of multiwalled carbon nanotubes causes reduction of relative density of the sinters. The other authors [9, 10] observed density in the range from 8.8 g/cm^3 to 9.45 g/cm^3 for silver based materials with addition of graphite. Low density of the produced composites results mainly from lower density of carbon nanotubes in relation to graphite.



A – mechanically milled and sintered by SPS method,

B – electroless deposited and sintered by SPS method,

C – reduced with $NaBH_4$ and sintered by SPS method.

Fig. 8. Density and electrical conductivity of sinters depending on the carbon nanotubes content and method of powder production

Electrical conductivity of the produced materials depends on CNTs content and on the method of powder preparation. High content of CNTs in the composite causes significant reduction of electrical conductivity, as observed in Ag-3wt% CNT sinter, prepared by high-energy milling (Fig. 8). It results among others from microstructure of the material, in which volume content of carbon forms is very high in relation to silver, and from the lowest density. The electrical conductivity was in the range from 48.36 to 56.72 MS/m for the composite with 0.3wt% CNT, whereas for 0.1wt% CNT it was at the level from 54.02 to 57.96 MS/m depending on the method of powder production. The conductivity values are lower for powder prepared by electroless deposition, what may result from presence of residues of the chemical compounds used for the powder production, e.g. $SnCl_2$, $PdCl_2$ – having influence on the reduction of electrical conductivity.

Electrical properties of the composites were examined to evaluate arc erosion resistance of the produced materials. The studies were carried out under model conditions and consisted of the mass loss measurements performed after every switching cycle ($\Delta m = f(n)$). The following parameters were applied in the tests: current – 10 A, voltage – 500 V, arc time – 10 ms, number of switching – 50 000.

The quantitative comparisons of tested materials indicated the influence of both quantity of doped material and method for its production on the material properties.

The highest mass loss was observed in powder prepared by high-energy milling (Ag-3 wt% CNT). The mass loss was at the level of 17.1 mg after 50,000 switches. In the material, sintered with powder prepared by electroless deposition, with increase of CNTs addition the material loss increased from 1.3 to 3.4 mg. The highest arc erosion resistance was observed in the material sintered from powder after chemical reduction. In the case of material with 1 and 0.3 wt% CNT mass loss was at the level of about 1.5 mg after 50,000 switching cycles. For comparison, Fig. 9 presents the mass loss for material containing graphite particles in the silver matrix. The man-

ufacturing procedure of the reference material with graphite included powder mixing and then sintering (SPS) at the same parameters as for the tested composites. This material with graphite content of 0.1 and 0.3 wt% was characterized by significantly higher mass loss when compared to materials with addition of CNT (2.6 and 3.2 mg, respectively).

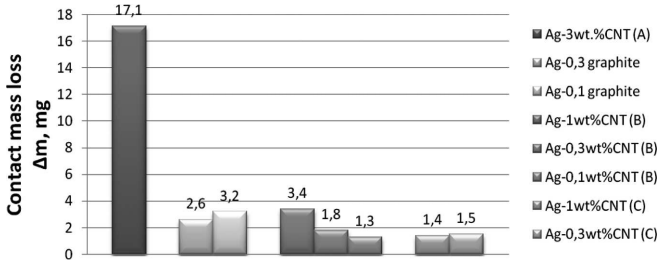


Fig. 9. Total mass loss of the sintered materials after 50 000 switching cycles

4. Summary

The article presents methods for production of silver based composite material with addition of carbon nanotubes with application of Spark Plasma Sintering method (SPS).

The developed technological processes, especially electroless deposition, result in a homogeneous distribution of multiwalled carbon nanotubes among silver particles and in metal (Ag) matrix after Spark Plasma Sintering. Preparation of composite powders (milling, electroless deposition and chemical reduction) influences their density, electrical conductivity and mass loss after electroerosion tests.

Electroerosion tests showed that addition of nanotubes improve material resistance to wear during cyclic current load. The materials show high stability during the operation.

The performed studies confirmed that silver based nanocomposites have strong potential for application in electrical engineering – especially in the electrical contacts.

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