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# COMPARISON OF PROPERTIES OF SILVER-METAL OXIDE ELECTRICAL CONTACT MATERIALS

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*Abstract*

*Changes in physical properties such as density, porosity, hardness and electrical conductivity of the Ag-$SnO_2$ and Ag-$SnO_2In_2O_3$ electrical contact materials induced by introduction of metal oxide nanoparticles were investigated. Properties of the obtained silver- metal oxide nanoparticle composites are discussed and presented in comparison to their counterparts with the micro metal oxide particles as well as comparable Ag-$SnO_2WO_3$ and Ag-ZnO contact materials. Studied silver-metal oxide composites were produced by powder metallurgy method from very fine pure silver and micro- and nanoparticle metal oxide powders. Very uniform microstructures were obtained for all investigated composites and they exhibited physical properties that are comparable with relevant properties of equivalent commercial silver based electrical contact materials. Both Ag-$SnO_2$ and Ag-$SnO_2In_2O_3$ composites with metal oxide nanoparticles were found to have lower porosity, higher density and hardness than their respective counterparts which can be attributed to better dispersion hardening i.e. higher degree of dispersion of metal oxide in silver matrix.*

*Keywords: silver based electrical contacts, metal oxide nanoparticles, powder metallurgy, physical properties*

## 1. Introduction

Electrical contact materials based on silver-metal oxide composites are very important functional materials which are commonly used in different low voltage

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switchgear devices such as contactors, relays, circuit breakers and switches [1-4]. Since electrical contact materials are used in diverse exploatation conditions, different types of silver based contact materials have been developed in order to meet the requirements for different applications. The usefulness of an electrical contact material is hence determined by a variety of electrical and mechanical properties, exploatation and load conditions it can withstand and economical reasons [4-6]. The essential properties for these materials from the performance point of view are high electrical and thermal conductivity, good mechanical properties as well as anti-welding behavior and oxidation resistance which would ensure preventing of erosion and welding of the contact by electric arc generated during switching operations.

Ever since Ag-$SnO_2$ and Ag-ZnO contact materials have emerged as an environmentally-friendly substitute for Ag-CdO they have been continually improved regarding their performance and applicability. Commercial production and application of the $AgSnO_2$ contact materials is limited by their rather poor over-temperature behavior due to high contact resistance caused by the coalescence of $SnO_2$ particles in surface layers and poor workability resulting from high hardness and larger particle size of $SnO_2$ owing to the traditional manufacturing process [7]. Nowadays, it is known that the functional properties of the Ag-$SnO_2$ electrical contact materials can be improved by addition of a second metal oxide component of such as $In_2O_3$, $Bi_2O_3$, CuO or $WO_3$ which increase dispersion of main oxides ($SnO_2$) in silver matrix and contribute to the activation of sintering process [8, 9]. It was found that small addition of $In_2O_3$ to Ag-$SnO_2$ causes foremost improvement of mechanical properties while keeping the good values of electrical conductivity. Alternatively, addition of $WO_3$ improves sinterability and wettability of $SnO_2$ in molten Ag thus improving the anti-welding and over-temperature behavior [9]. On the other hand, Ag-ZnO materials utilize the high melting point of ZnO resulting in that it's decomposing is more difficult than that of $SnO_2$ under the same exploitation conditions, thus preventing the appearance of holes, as well as the fact that the ZnO particles effectively protect against silver sputtering [10]. However, apart from possessing low contact resistance Ag-ZnO materials have unsatisfactory resistance to welding and greater tendency to contact wear [11].

In addition to the chemical composition, microstructure has the most important role in determining properties of electrical contact materials. Hence, a general course of action to improve the anti-welding behavior and wear resistance of these materials is to obtain uniform dispersion of metal oxide particles in a soft silver matrix. Generally speaking, when additives are used to alter the interaction of a silver matrix and base oxides thus altering the materials properties, finer microstructures are more favorable. Although, the influence of the oxide particle size on the switching behavior is still not well defined it is generally accepted that smaller metal oxide particles promote formation of anti-welding characteristics in the contact surface exposed to the arc upon

the solidification of the molten Ag. Moreover, under certain conditions erosion rate can be decreased by a decrease of the metal oxide particle size. When using smaller oxide particles, if there is sufficient wetting by the molten Ag to prevent formation of oxide layers the contact resistance can be considered not critical [12]. However, there is a limit to reduction of the particle size given that if the particle spacing is on the order of the mean free electron path of the conduction electrons a significant reduction in bulk conductivity can be expected. It was found that the optimal microstructure can be achieved by a homogenous distribution of metal oxide particles with diameters in range of 50-200 nm [12].

The influence of metal oxide nanoparticles on the microstructure and physical properties such as density, porosity, hardness and electrical conductivity of Ag-$SnO_2$ and Ag-$SnO_2In_2O_3$ electrical contact materials was investigated. Properties of the obtained silver-nanoparticle metal oxide composites are discussed and presented in comparison to their microparticle metal oxide counterparts as well as equivalent Ag-$SnO_2WO_3$ and Ag-ZnO contact materials.

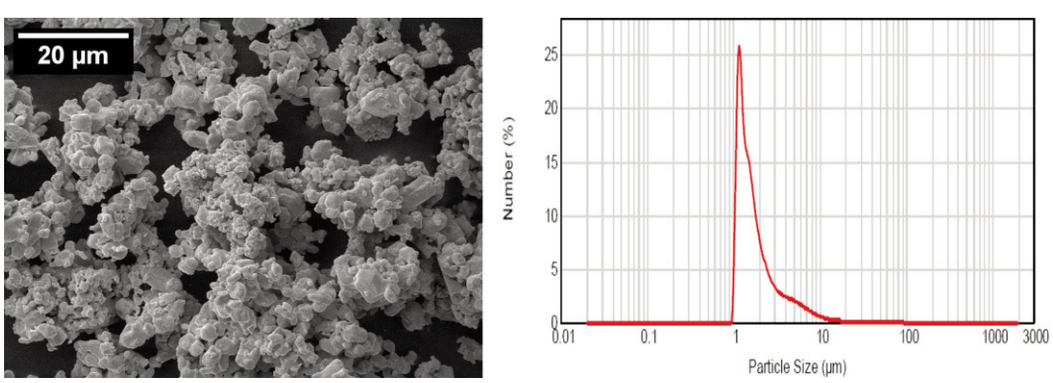
## 2. Experimental

### 2.1 Starting powders

Studied silver based electrical contact materials were produced by powder metallurgy (PM) method from pure silver powder obtained by chemical synthesis route and very fine commercial powders ($SnO_2$ - 99.9%, $In_2O_3$ - 99.99%, ZnO - 99.0%, $WO_3$ - 98.5%) as well as commercial $SnO_2$ and $In_2O_3$ nano powders produced by Sigma-Aldrich.

Silver powder of high purity was made via aqueous precipitation of pure silver from silver nitrate by mixing of solutions of silver nitrate and sodium hydroxide with addition of formaldehyde. As particle size of precipitate is affected by reaction kinetics, processing conditions were carefully selected.

Particle size distribution of the produced silver powder was analyzed using Malvern Instruments laser diffractometer Mastersizer 2000 with the Scirocco 2000 module, while morphology was investigated by means of scanning electron microscopy (SEM). Corresponding SEM image and particle size distribution curve are presented in Fig. 1a and Fig. 1b, respectively.

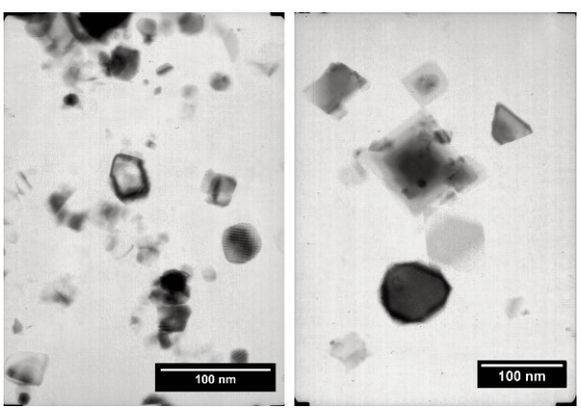



*a)* *b)*

*Figure 1. Obtained silver powder: a) SEM image and b) particle size distribution curve*

The particles show rather narrow size distribution with the mean particle size of the silver powder determined by laser diffractometry having following values: d(0.1) = 1.126 μm, d(0.5) = 1.521 μm and d(0.9) = 4.237 μm.

Particle size and shape of the used commercial $SnO_2$ and $In_2O_3$ nano powders was analyzed by means of transmission electron microscopy (TEM). The obtained TEM image of used $SnO_2$ nano powder (Fig.2a) reveals the particle size in range 20-50 nm, while TEM image $In_2O_3$ nano powder (Fig. 2b) demonstrates the particle size in range 50-100 nm.




*a)* *b)*

*Figure 2. – TEM images of used commercial nano powders: a) $SnO_2$ and b) $In_2O_3$*

## 2.2 Sample preparation and processing conditions

Powder metallurgy method (PM) was selected for preparation of the investigated samples since it provides uniform microstructure, high electrical conductivity and gives possibility for quick and easy production of samples with a variety of chemical compositions i.e. possibility of production of silver based composites containing two or more metal oxides. Compositions of the prepared samples are given in Table 1.

*Table 1 – Composition of the investigated silver-metal oxide electrical contact materials*

| No | Sample | Composition | | | | |
|---|---|---|---|---|---|---|
| | | Ag | $SnO_2$ | $In_2O_3$ | $WO_3$ | ZnO |
| 1 | Ag-$SnO_2$ | 92 | 8 | - | - | - |
| 2 | Ag-$SnO_2$ nano | 92 | 8 | - | - | - |
| 3 | Ag-$SnO_2In_2O_3$ | 89.1 | 8 | 2.9 | - | - |
| 4 | Ag-$SnO_2In_2O_3$ nano | 89.1 | 8 | 2.9 | - | - |
| 5 | Ag-$SnO_2WO_3$ | 90 | 9.5 | - | 0.5 | - |
| 6 | Ag-ZnO | 92 | - | - | - | 8 |

The technological procedure included dry and wet homogenization of powder mixtures, pressing, sintering, additional mechanical treatment (forging) and characterization. Since the starting powders were in the form of agglomerates consisting of very fine particles, homogenization both wet and dry was done in several steps. Uniformity of the obtained mixtures was controlled using scanning electron microscopy. The samples were pressed into tablets Ø16 × 3 mm by hydraulic press under the pressure of 100 MPa in a steel dye. The samples were sintered for 2h at 800°C in electro-resistive oven with programmable digital temperature controller with the accuracy ±1°C in the air atmosphere. After sintering, the samples were forged (at 800°C) with the low degree of reduction (~15%). Subsequently the samples were annealed at 750°C for 30 min and then quenched in water.

### 2.3 Characterization

Microstructure of the samples after sintering and mechanical treatment and chemical composition of the observed phases were studied on polished cross-section surfaces using JEOL JSM-6610LV scanning electron microscope equipped with Oxford Instruments energy dispersive spectrometer (EDS). Density of the obtained samples was determined by standard methods. Applying the procedure given in more detail in [13] theoretical density of samples was calculated and by comparison between experimental and theoretical densities the porosity of samples was determined.

Theoretical density of composites, $\rho_t$, was calculated according to relation [13-15]:

$$\rho_t = \left(1 - V_f\right)\rho_m + V_f \rho_f \tag{1}$$

where $V$ is volume fraction, $\rho$ – density while $f$ and $m$ indexes correspond to filler (metal oxide powder) and matrix (silver powder), respectively.

Porosity of the investigated composites, $\tau$, was determined by comparison of experimental and theoretical densities of the samples according to relation [13-15]:

$$\tau = \left(\frac{\rho_t - \rho_e}{\rho_t}\right) \times 100 \tag{2}$$

where $\rho_e$ – is experimentally obtained value of composite density.

Hardness measurements were carried out after sintering and mechanical treatment on polished samples at room temperature using a Vickers hardness tester applying load of 5 kp. The reported hardness values are an average of three readings. Electrical conductivity of the investigated materials was measured using Foerster SIGMATEST 2.069 eddy current instrument for measurements of electrical conductivity of non-ferromagnetic metals based on the complex impedance of the measuring probe, with the 8 mm probe.

## 3. Results and discussion

Microstructures of the investigated silver-metal oxide electrical contact materials are illustrated by SEM images (Fig.3) of the polished cross-sections of the produced samples after sintering, mechanical treatment and subsequent annealing. The presented images demonstrate that homogeneous distribution of the metal oxide particles in the silver matrix i.e. very uniform microstructures with reasonably small porosity were obtained for all investigated materials. This is important from the point of view that uniformly dispersed oxide particles can strengthen the otherwise soft silver matrix resulting in higher hardness, improved anti-welding behavior and wear resistance.

Combined SEM-EDS analysis provided better insight into the microstructure of the investigated silver based electrical contact materials. Considering that secondary electron SEM images provide more information regarding the topography and morphology i.e. almost 3d images of the observed surfaces, they were used to illustrate presence of pores in the obtained microstructures. The EDS analysis was used for determination of the composition of the observed phases and the identified phases are

marked on presented figures.

Fig.4 shows microstructures of the Ag-$SnO_2$ composite material with micro (sample 1) and nano metal oxide particles (sample 2). As suggested by Fig. 3a and Fig. 3b, the microstructures of the sample 1 and sample 2 are quite similar. Only at higher magnifications differences in microstructure become apparent, as it is illustrated by an enlarged detail of the obtained microstructure of the sample 2 given in Fig 4b which reveals better dispersion of $SnO_2$ nanoparticles in silver matrix and lower porosity of the composite.

More noticeable differences between the microstructures can be observed on the

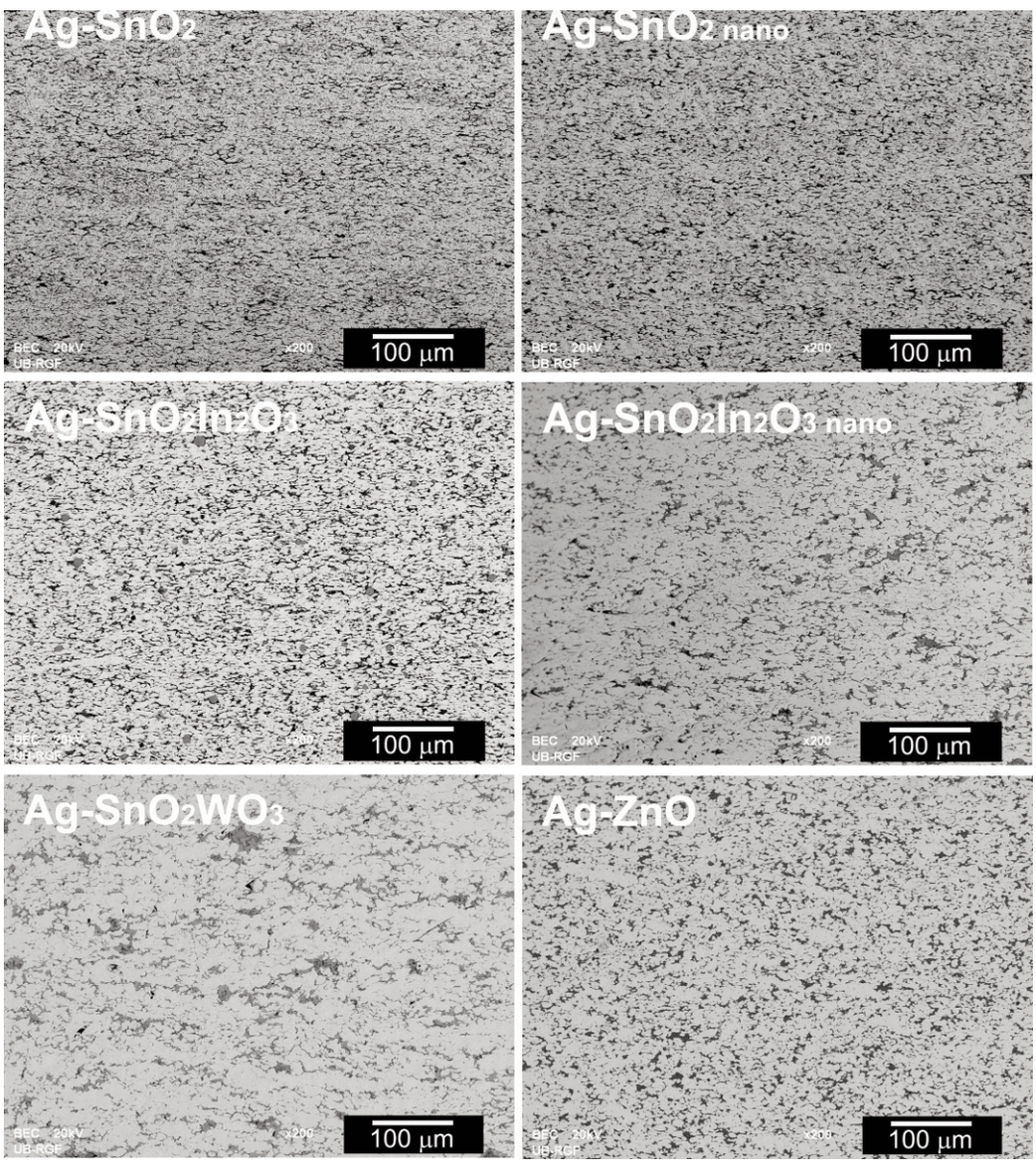
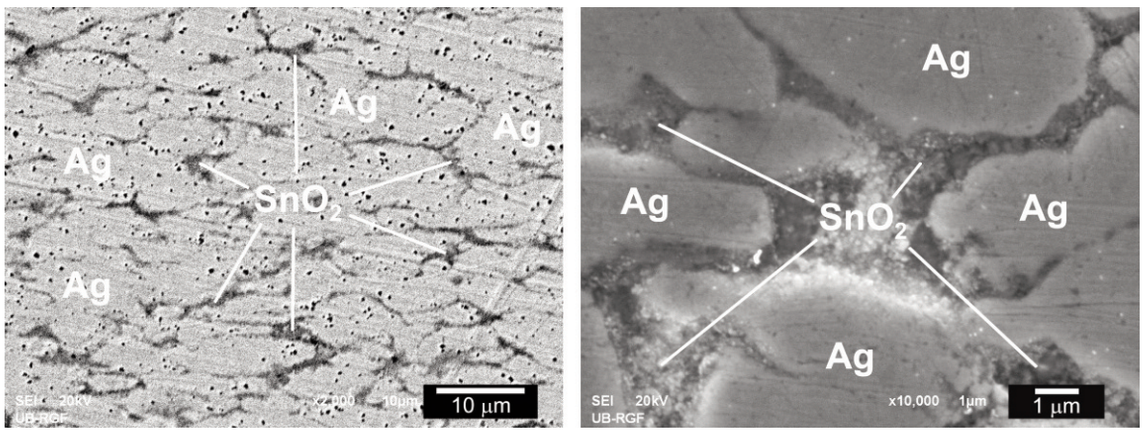



*Fig. 3– SEM metallographic images of the polished cross-sections of the investigated silver-metal oxide composites*



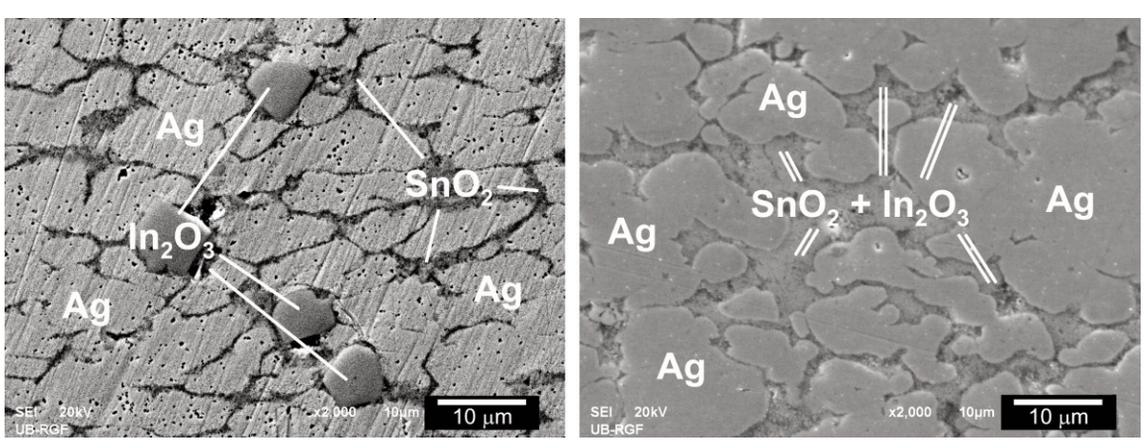

*a)* *b)*

*Fig. 4. SEM images with results of EDS analysis of $AgSnO_2$ samples with a) micro (sample 1) and b) nano metal oxide particles (sample 2)*

images of the Ag-$SnO_2In_2O_3$ samples with micro and nano metal oxide powders presented in Fig.5a and Fig.5b, respectively. Besides the obvious absence of the coarse $In_2O_3$ particles, the microstructure of the sample with nano metal oxide powders given in Fig. 5b appears to be much finer and less porous. Better connectivity of the silver grains can be observed as well.

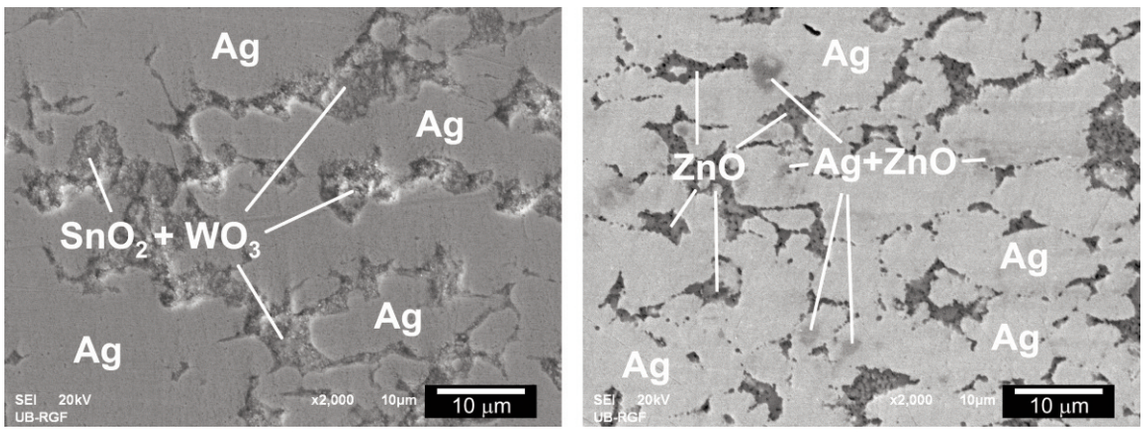
Microstructures of the investigated Ag-$SnO_2WO_3$ (sample 5) and Ag-ZnO (sample 6) materials are illustrated by secondary electron SEM images presented on Fig. 6 with marked chemical compositions. Fig. 6a demonstrates more or less the same structure of the sample as of the other analyzed samples, with $SnO_2$ and $WO_3$ particles situated predominantly on silver grain boundaries.

However, in contrast to other investigated materials, within microstructure of the sample 6 (Fig. 6b) zinc oxide particles that




*a)* *b)*

*Fig. 5. SEM images with results of EDS analysis of Ag-$SnO_2In_2O_3$ samples with a) micro (sample 3) and b) nano metal oxide particles (sample 4)*




*a)* *b)*

*Fig. 6. SEM images with results of EDS analysis of a) Ag-$SnO_2WO_3$ (sample 5) and b) Ag-ZnO (sample 6)*

are present in the silver matrix can be found both on grain boundaries and dispersed inside the silver grains. Given that prior to sintering, during mixing and pressing stages, the contact surfaces between powder particles are plentiful of pores and defects some of the finer ZnO particles could be wedged between larger Ag particles. Some of these contact surfaces will turn into grain boundaries and some will disappear gradually during sintering [16], hence enclosing ZnO particles inside the grain. Consequently, this provides an increase of the degree of dispersion which could lead to an improvement in material's performance.

The physical properties of the investigated contact materials after sintering, mechanical treatment and subsequent annealing are compared in Table 2.

It can be noticed that the relatively high values of electrical conductivity were obtained despite the existence of porosity in the materials (Table 2.). Particularly since pores are potential scattering centers for the electrons and consequently reduce conductivity [17]. Furthermore, good values of hardness can be attributed to the high density and very uniform distribution of the metal oxides in silver matrix.

Both materials containing metal oxide

*Table 2. Physical properties of the investigated contact materials*

| No | Sample | Density [g/cm$^3$] | Porosity [%] | Hardness [HV] 5 kP | Electrical conductivity [% IACS] |
|---|---|---|---|---|---|
| 1 | Ag-$SnO_2$ | 9.37 | 7.08 | 68 | 68.61 |
| 2 | Ag-$SnO_2$ nano | 9.89 | 1.95 | 81 | 56.11 |
| 3 | Ag-$SnO_2In_2O_3$ | 9.4 | 6.14 | 73 | 53.02 |
| 4 | Ag-$SnO_2In_2O_3$ nano | 9.54 | 4.74 | 75 | 56.98 |
| 5 | Ag-$SnO_2WO_3$ | 9.32 | 7.33 | 71 | 52.63 |
| 6 | Ag-ZnO (92-8) | 9.61 | 2.08 | 82 | 66.63 |

nanoparticles (samples 2 and 4) exhibit higher values of hardness than their counterparts (samples 1 and 3). The observed enhancement of hardness (Table 2.) can be attributed to a greater dispersion hardening of soft silver matrix by the dispersed oxide phase nanoparticles. This assumption is supported by the SEM images of the corresponding microstructures presented on Fig. 4 and Fig. 5 which also demonstrate better dispersion of metal oxide nanoparticles.

Higher value of electrical conductivity of the sample 1 containing micro $SnO_2$ particles (Table 2.) can be explained by lower dispersion of metal oxide particles and existence of connected pure silver grains (oxide free zones) which would attribute to higher electrical conductivity on one side but also derogate mechanical properties on the other, as it is illustrated by lower values of hardness.

Favorable physical properties and very good electrical performance exhibited by the investigated Ag-ZnO contact material (sample 6 in Table 2.) can be ascribed to greater dispersion of very fine ZnO particles in silver matrix as it is illustrated by the corresponding SEM image of the sample 6 microstructure presented on Fig. 6b.

It should be pointed out that besides chemical composition and particle size processing conditions play a very important role in determining final properties of the PM produced materials [18]. The significant influence of the sintering regime and mechanical treatment on the electrical conductivity of the investigated silver metal oxide composites is demonstrated on Fig. 7, illustrating difference in electrical conductivity of green compacts and samples after applied sintering regime and subsequent forging.

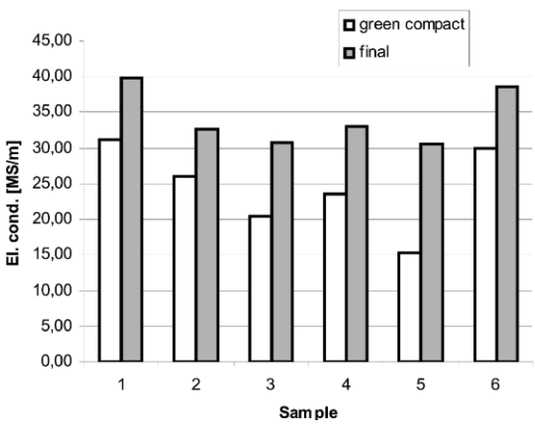



*Fig. 7. Electrical conductivity of the investigated silver metal oxide composites before and after sintering and subsequent mechanical treatment*

Considering that it well known that apart from sintering regime applied pressure during consolidation stage determines physical properties of materials (porosity, bulk density and hardness) further enhancement of materials properties is possible by application of higher pressure for sample processing. Many published studies suggest that pressure even up to 900 MPa [10] can be applied.

The presented experimentally obtained results of microstructural analysis and determined mean values of density, hardness and electrical conductivity of the investigated electrical contact materials are comparable to each other and at the same time comparable to the same characteristics of the equivalent commercially available electrical contact materials, particularly Ag-CdO. This is significant, considering that the

existing EU directives (RoHS, WEEE) restrict the use of potentially hazardous substances among which Cd and necessitate introduction of more environmentally friendly electrical contact materials such as silver-metal oxide composites investigated in this study.

## 4. Conclusion

The influence of metal oxide nanoparticles on microstructure and physical properties such as density, porosity, hardness and electrical conductivity of the Ag-$SnO_2$ and Ag-$SnO_2In_2O_3$ electrical contact materials was investigated. Properties of the obtained silver- nanoparticle metal oxide composites are discussed and presented in comparison to their counterparts with the micro metal oxide particles as well as comparable Ag-$SnO_2WO_3$ and Ag-ZnO contact materials. The microstructural analysis revealed that very uniform microstructures of the all investigated composites were obtained. This resulted in density, hardness and electrical conductivity of the all investigated composites being comparable with relevant properties of equivalent commercial silver based electrical contact materials. Another important point is that the analyzed properties of the investigated materials are in the same range of values as those of Ag-CdO, particularly since they are considered as its more environmentally friendly substitute. In comparison to materials with micro oxide particles, both Ag-$SnO_2$ and Ag-$SnO_2In_2O_3$ composites with metal oxide nanoparticles are less porous and exhibit higher degree of dispersion of metal oxide in silver matrix. Moreover, the both materials containing metal oxide nanoparticles possess higher values of hardness and density than their respective counterparts. The observed enhancement of hardness can be attributed to a greater dispersion hardening of otherwise soft silver matrix by the dispersed oxide phase nanoparticles. High hardness and very good electrical performance exhibited by the investigated Ag-ZnO contact material can be ascribed as well to the greater dispersion of very fine metal oxide particles in silver matrix. This is very significant especially from an application point of view considering that better dispersion of oxides and higher hardness can improve anti-welding behavior and wear resistance.

It is expected that the differences in properties and performance of investigated electrical contact materials with micro- and nano- metal oxide particles will become more apparent after further tests on surface erosion and welding resistance which would illustrate the benefits of introduction of metal oxide nanoparticles in silver matrix to the full extent.

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