

## Electrical contact materials based on silver

*Composite electrical contact materials based on silver and oxides of different metals have been used for many years in different types of electrical devices for making and breaking of electrical circuit. Ag-CdO materials have been most commonly used over the years as the materials for electrical contacts and other electrical components due to their excellent electrical and mechanical properties, mainly for small and medium-current loads. Recent investigations have led to the development and implementation of new environmentally friendly electrical contact materials in which the toxic CdO is replaced by less harmful metal oxides, while maintaining the good final properties. It was found that the Ag-SnO<sub>2</sub> composite material meets most of the required properties. Results of experimental investigations of different technological procedures for obtaining various types of silver based electrical contact materials are presented in this paper through defined technological phases with optimized process parameters. The structural, mechanical and electrical characteristics of the investigated and realized contact materials are presented as well. The examples of materials applications are given and illustrated.*

**Key words:** Electrical contacts, silver-metal oxides, processing, properties

### INTRODUCTION

Electrical contact materials based on silver and oxides of different metals have been used for many years for different electrical equipment which work with different cuts of electrical circuit. A majority of contact applications in industry utilize silver-type contacts, since silver has the highest electrical and thermal conductivity of all metals. This type of electrical contacts include pure metal, alloys, and mixtures of metal and metal oxide powders. Also, silver is used as a plated, brazed, or mechanically bonded overlay on other contact materials - notably, copper and copper-base materials. Since electrical contact materials are used in diverse exploitation 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 also determined by a variety of electrical and mechanical properties, exploitation and load conditions it can withstand and economical reasons [1-4].

For many years silver - cadmium oxide (Ag-CdO) has been the preferred material for electrical contacts used in different low-tension devices of contactors type due to its outstanding functional properties: high electrical and thermal conductivities, high resistance to arcing, high welding adhesion resistance, low contact resistance, high hardness and strength and thus low erosion both in make and brake operations [5-8].

The two most common routes for production of silver-cadmium oxide electrical contact materials are based on powder metallurgy methods (PM) and internal oxidation (IO) of Ag-Cd alloys. The goal of optimization of process parameters for the both production methods is obtaining of good and homogeneous oxide dispersion within the silver matrix, since it is known that antiwelding behavior and wear resistance can be improved by uniform dispersion of the metal oxide particles in soft silver matrix [9].

The obtained experimental results of investigation of Ag-CdO electrical contact materials will be used to demonstrate and discuss internal oxidation production process. In general, the oxidation rate depends on the Cd content in the Ag-Cd alloy, purity of the starting alloying components, diffusion of oxygen through the oxide layer and the purity of the formed oxide. Temperature and duration of oxidation are two most influential parameters for the oxidation rate and thickness of the oxide layer. Furthermore the oxidation rate and the thickness of the oxide layer, in the same temperature and time interval can be influenced by the oxygen pressure. The process of occurs in the following manner: oxygen diffuses into an alloy and causes sub-surface precipitation of the oxides of one or more alloying elements, essentially it dissolves in the base metal and diffuses inward through the metal matrix containing previously precipitated oxide particles [10]. The results of investigation of oxidation layer thickness dependence on the temperature and time of inner oxidation for the

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Ag-Cd alloys with different content of Cd are presented in this paper.

Based on the EU regulative considering toxicity of most commonly used metal-oxide CdO, further investigations of electrical contact materials are directed towards replacement of the toxic and harmful CdO with non toxic oxides dispersed in silver matrix, in order to obtain the new more environmentally friendly electrical contact materials, which would have many advantages from the technical, economical and environmental point of view [4,11]. In the recent years, Ag-SnO<sub>2</sub> has emerged as the most promising material i.e. material that possesses the majority of the required functional properties. Nowadays, it is known that electrical and mechanical properties of Ag-SnO<sub>2</sub> electrical contact materials can be improved by adding small amounts of In<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, CuO and WO<sub>3</sub> [11,12]. These additives increase dispersion of main oxides (SnO<sub>2</sub>) in silver matrix and contribute to the activation of sintering process in order to gain optimal microstructure, which results in improved electrical and mechanical properties.

The obtained experimental results of investigation of Ag-SnO<sub>2</sub> electrical contact materials will be used to demonstrate and discuss technological procedure of production of investigated materials by powder metallurgy method (PM). The relation between synthesis conditions, microstructure, electrical and mechanical properties of the electrical contact materials based on Ag-SnO<sub>2</sub> with different SnO<sub>2</sub> content and the influence of addition of small amount of In<sub>2</sub>O<sub>3</sub> on the dispersion of main oxide SnO<sub>2</sub> in silver matrix and therefore on improvement of electrical and mechanical properties was discussed as well.

## EXPERIMENTAL

Process of inner oxidation of Ag-Cd alloys with amount of Cd of 9.5, 11, 12 and 16 mass % was investigated. Ag-Cd alloys synthesized by melting of pure metals (99.90 mass %) Ag and Cd were plastically deformed on low temperatures. Inner oxidation of the investigated alloys was done in electro resistive oven. For all mentioned alloys oxidation was conducted in air atmosphere under natural convection of air at the temperatures 670°C, 750°C and 795°C during 5; 9.5; 20.5; 36 and 48 hours. Measurements of thickness of oxidized layer were done on the metallographic microscope REICHART of POLYVAR – MET type. Vickers hardness (applying load of 5 kp) was measured after the applied oxidation regimes.

Studied electrical contact materials based on Ag-SnO<sub>2</sub> with 8, 10, and 12 mass% of SnO<sub>2</sub> and Ag-SnO<sub>2</sub>

with small addition of In<sub>2</sub>O<sub>3</sub> (2.9 mass%) were produced by powder metallurgy (PM) method from pure powders (Ag - 99.9%, SnO<sub>2</sub> - 99.9%, In<sub>2</sub>O<sub>3</sub> - 99.99%). The technological procedure included preparation of powders, dry and wet homogenization of powder mixtures, pressing, sintering, additional mechanical treatment (forging and rolling) and characterization.

The silver powder was obtained by chemical synthesis route while SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> powders are the commercial powders produced by Merck. Since the starting powders were in the form of agglomerates consisting of very fine submicron particles, homogenization both wet and dry was done in several steps. Uniformity of the obtained mixtures was controlled using scanning electron microscopy (SEM). The samples were pressed into 80×20×5 mm plates by hydraulic press under the pressure of 98 MPa in a steel die. In order to provide good bond between the contact material and contact holder by soldering, about 25% of the total thickness of the electrical contact, on the side facing the holder, should not contain metal oxide i.e. should only contain pure silver matrix. The samples were sintered in electro-resistive oven with programmable digital temperature controller with the accuracy ±1°C in the air atmosphere. The applied sintering regimes are presented on Fig. 1.

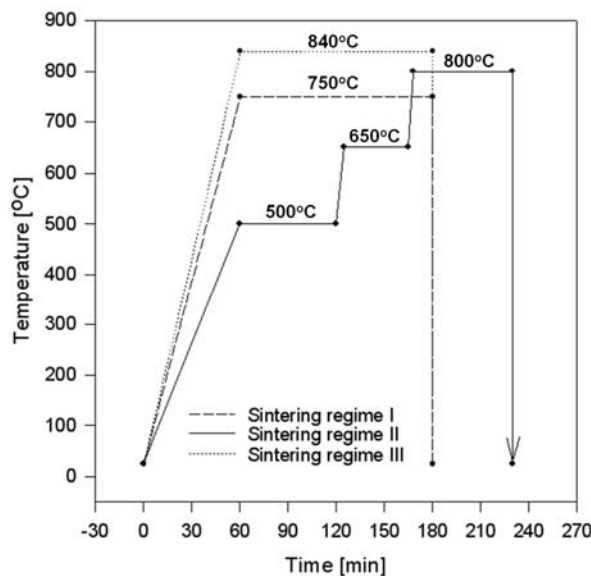


Fig. 1. Applied sintering regimes in sintering process of investigated Ag-SnO<sub>2</sub> and Ag-SnO<sub>2</sub> In<sub>2</sub>O<sub>3</sub> electrical contact materials

After sintering, the samples were forged and hot rolled with the low degree of reduction to the final thickness of 2 mm. Microstructure of the samples was observed on polished and etched cross-section

surfaces using the metallographic light microscope Leica DM ILM. Density of the samples was determined by standard methods (ASTM B 311-93 (2002) e1). Vickers hardness (applying load of 5 kp) was measured after the applied sintering and mechanical treatment regimes.

Electrical conductivity of the both investigated materials (Ag-CdO, Ag-SnO<sub>2</sub>) 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.

## RESULTS AND DISCUSSION

Graphic dependence of thickness of oxidized layer for different Cd content in Ag-Cd alloys in applied oxidation regimes is presented on Fig. 2. After comparing of changes of thickness of oxidized layer with temperature and time, it is obvious that oxidation rate is the highest for the alloy with the least amount of Cd and the lowest for the alloy with highest amount of Cd. At the same time, according to the results presented in Fig. 2 it can be observed that at higher temperatures (795°C) inner oxidation rate is higher. Hence, for applied synthesis conditions the temperature has the highest influence on the process of inner oxidation.

Electrical contacts based on Ag-CdO are less plastic (higher hardness) comparing to Ag-Cd alloy. Hardness of oxidized layer of alloy is not the same on the whole profile. It is the highest on the surface, and it decreases with increase of distance from the surface

At the certain distance from the surface hardness is constant and rapidly decreases at the border of oxidized and non-oxidized layer. Mean value of hardness after applied inner oxidation regimes is 80 HV for 9.5 mass% of Cd; 85 HV for 11 mass% of Cd; 91 HV for 12 mass% and 130 HV for 16 mass% of Cd. It was found that the content of 9-12 mass % of CdO in the Ag-CdO alloys effectively influences the decrease of deformation and destruction of electrical contacts. With higher concentrations of CdO, above 12 mass%, possibility of inner breaking due to inner tension caused by increase of grains diameter after oxidation increases.

The influence of temperature and time of oxidation on thickness of oxide layer in investigated Ag-CdO electrical contact materials is illustrated by characteristic optical micrographs of cross-sections presented on Fig. 3.

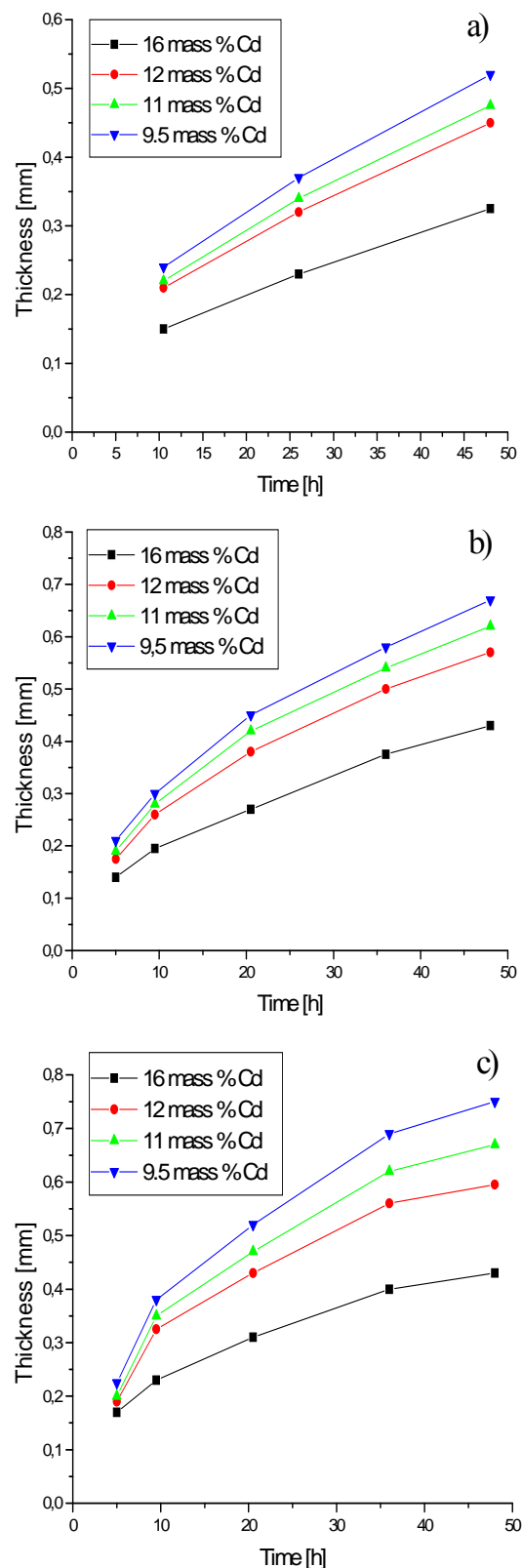


Fig. 2. Dependence of thickness of oxidized layer for Ag-Cd alloys with different Cd content: inner oxidation on a) 670°C, b) 750°C and c) 795°C

% Cd	<i>Inner oxidation of Ag–Cd alloys with different Cd content</i>					
	670°C		750°C		795°C	
	5h	48h	5h	20.5h	5h	33h
9%						
12%	22h		20.5h		33h	
16%	5h	48h	5h	48h	5h	46.5h

Fig. 3. Characteristics optical micrographs of Ag–CdO electrical contact materials experimentally obtained by inner oxidation on different temperatures and time

In the optimized process of oxidation high and homogenous dispersion of CdO in the silver matrix is obtained (Fig. 4). Metallographic investigation have shown that the minimal thickness of oxide layer is about 66% of the total thickness of the Ag–Cd plate and that the average thickness of the oxide layer, depending upon the temperature and duration of oxidation process is about 68–72 %. In order to provide good bond between the contact material and contact holder by soldering, about 25% of the total thickness of the electrical contact material must not be oxidized, as illustrated on Fig. 4.

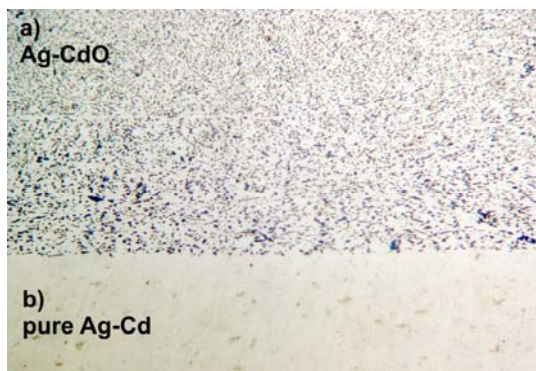


Fig. 4. Cross section of the Ag–CdO<sub>11</sub> obtained by inner oxidation: oxide layer, b) pure Ag–Cd layer

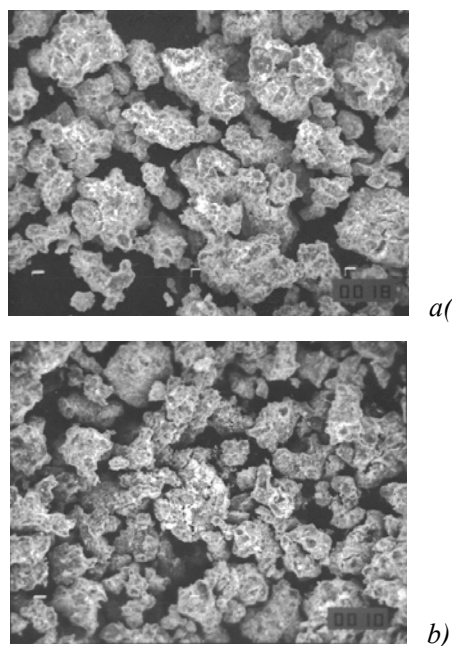


Fig. 5. SEM images ( $\times 500$ ) of a) Ag–SnO<sub>2</sub>, and b) Ag–SnO<sub>2</sub> In<sub>2</sub>O<sub>3</sub> mixtures

Electrical conductivity of the investigated Ag–CdO electrical contact materials is in the range from 45 – 52 MS/m.

The PM process of production of electrical contact materials is illustrated by the following experi-

mental results of investigation of Ag-SnO<sub>2</sub> electrical contact materials.

The SEM images of the Ag-SnO<sub>2</sub> (92:8) and Ag-SnO<sub>2</sub> In<sub>2</sub>O<sub>3</sub> (87.8:9.30:2.90) mixtures that were used in investigation are presented on Fig. 5.

By continuous microscopic control of process of homogenization it was determined that despite the formation of agglomerates, due to very fine particles of the powders used, the good uniformity of mixtures was obtained, which has provided reasonable values of density in the subsequent process of consolidation.

Metallographic images of microstructures (polished cross-sections) of the investigated Ag-SnO<sub>2</sub> (92:8) electrical contact materials after the applied sintering regimes and additional mechanical treatment are shown on Fig. 6. The presented cross-sections are with and without Ag layer.

The obtained microstructures of the investigated Ag-SnO<sub>2</sub> In<sub>2</sub>O<sub>3</sub> (87.8 : 9.30 : 2.90) electrical contact materials after different sintering regimes and mechanical treatment are presented on Fig. 7.

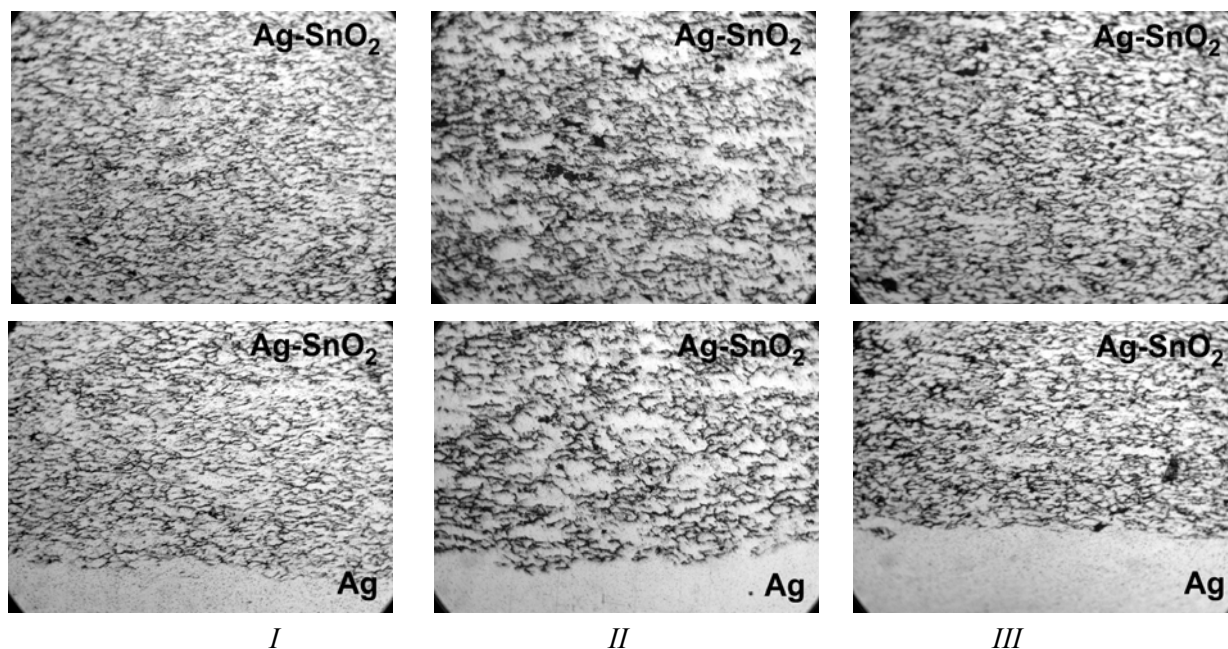


Fig. 6. Microstructure (cross-section) ( $\times 500$ ) of Ag-SnO<sub>2</sub> (92:8) sintered at regimes I, II, III and additionally mechanically treated

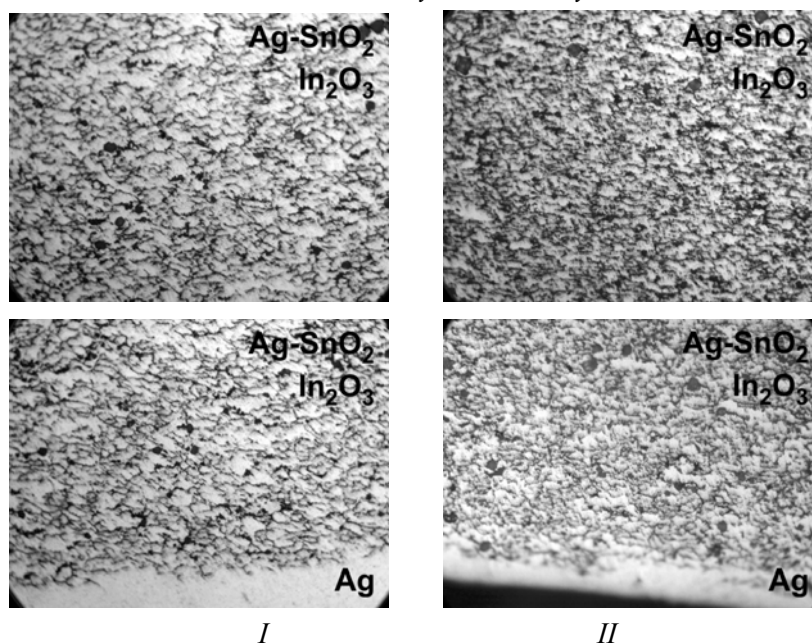


Fig. 7. Microstructure (cross-section) ( $\times 500$ ) of Ag-SnO<sub>2</sub> In<sub>2</sub>O<sub>3</sub> (87.8: 9.30: 2.90) after sintering at regimes I, II and additional mechanical treatment

Since the investigated electrical contact materials were produced from very fine powders, which have a high specific surface and good sinterability, the obtained microstructure was homogenous and the porosity was very low. From Fig. 6. and Fig. 7. it can be seen that the components  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  are uniformly dispersed in silver matrix. Although, the Ag-SnO<sub>2</sub> 92:8 (Fig. 6) samples were sintered in three different regimes, fairly similar morphologies of the "net" type (distribution of the oxide in silver matrix in the net pattern) can be observed. Slightly higher concentration of the  $\text{SnO}_2$  in the "net" walls is evident for the sample sintered in multi stage sintering regime (Fig.6 regime II). Furthermore, this sample has the highest hardness (HV 91.6). This can be explained by the enlargement of oxide grains and the increase of its

concentration in the net walls due to the multi stage sintering regime and longer sintering time and since the oxide has higher hardness in regard to silver matrix this can be the reason of the higher hardness of this sample compared to the other two investigated electrical contact materials.

Resistance to the erosion of the investigated Ag-CdO and Ag-SnO<sub>2</sub> electrical contacts measured as a contact mass change resulting from on and off switching of alternating current. The obtained results correspond to the previously published results [4,11].

Summarized experimental results of density, hardness and electrical conductivity measurements of investigated Ag-CdO and Ag-SnO<sub>2</sub> electrical contact materials are presented in the Table 1.

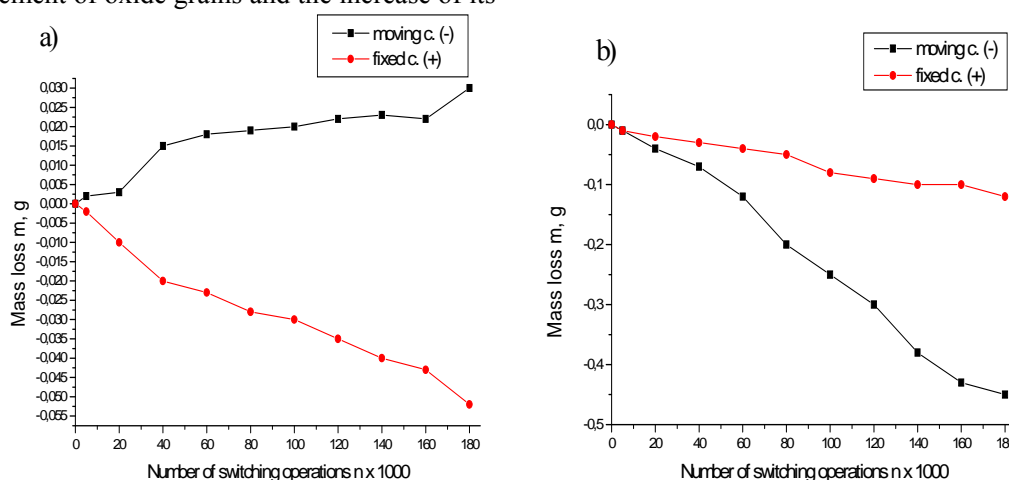


Fig. 7. Wear of the a) Ag-CdO and b) Ag-SnO<sub>2</sub> contacts in dependence of switching operations

Table 1. Mean values of density, hardness and electrical conductivity of investigated electrical contact materials with corresponding synthesis conditions

Sample	Ag [mass%]	CdO [mass%]	Time [h]	Temperature [°C]	Density [g/cm <sup>3</sup> ]	Hardness [HV/5kp]	Electrical Conductivity $\sigma$ , [MS/m]
IO Ag-CdO	91.5	9.5			10.0	80	50
	89	11			10.1	85	52
	88	12			10.1	91	48
	84	16			10.2	130	45
PM Ag-SnO <sub>2</sub>	Ag [mass%]	SnO <sub>2</sub> [mass%]	In <sub>2</sub> O <sub>3</sub> [mass%]	Sintering regime	Density [g/cm <sup>3</sup> ]	Hardness [HV/5kp]	Electrical Conductivity $\sigma$ , [MS/m]
	88.0	12.00	—	I	7.2	73.2	26.98
	90.0	10.00	—	I	7.9	73.6	33.32
	92.0	8.00	—	I	7.4	70.8	35.75
	92.0	8.00	—	II	9.6	91.6	36.04
	92.0	8.00	—	III	9.8	102.0	38.57
	87.8	9.30	2.90	I	9.0	77.2	27.13
	87.8	9.30	2.90	II	9.4	84.2	30.75

\*DODUCO, METALOR: AgSnO<sub>2</sub> (8, 10, 12);  $\rho = 9.4 - 10.3 \text{ g/cm}^3$ ; HV = 40 – 100 kp/m<sup>2</sup>;  $\sigma = 30 - 45 \text{ MS/m}$   
 AgCdO (10, 12, 13, 15);  $\rho = 9.9 - 10.3 \text{ g/cm}^3$ ; HV = 60 – 130 kp/m<sup>2</sup>;  $\sigma = 28 - 50 \text{ MS/m}$

The presented experimentally obtained results of microstructural analysis and determined mean values of density, hardness and electrical conductivity of the both investigated electrical contact materials are comparable to each other and at the same time comparable to the same characteristics of the commercially available electrical contact materials. For the Ag-SnO<sub>2</sub> electrical contact material maximal values of density, hardness and electrical conductivity were obtained with 8 mass% of SnO<sub>2</sub> after sintering at 840°C for 2 hours (sintering regime III) and additional mechanical treatment. Good results of density and hardness and consequently electrical conductivity were achieved for the Ag-SnO<sub>2</sub> with addition of In<sub>2</sub>O<sub>3</sub> (2.9 mass%) as well, since the small amounts of In<sub>2</sub>O<sub>3</sub> have obviously increased dispersion of main oxide in silver matrix and contributed to the activation of sintering process.

## CONCLUSION

The presented study gives brief overview of the the electrical contact materials based on silver with emphasis on the Ag-CdO and its more environmentally friendly substitute Ag-SnO<sub>2</sub>. The two most common routes for production of silver-metal oxide electrical contact materials internal oxidation (IO) and powder metallurgy methods (PM) were demonstrated and discussed on the example of synthesis and characterization of Ag-CdO and Ag-SnO<sub>2</sub>, respectively.

The of oxidation of Ag-Cd alloys with different content of Cd, was carried out in the atmosphere of air at applied temperatures and during defined time periods. The obtained experimental results of microstructure analysis revealed that thickness of oxidized layer is determined by temperature and duration of oxidation, amount of cadmium in Ag-Cd alloys and oxygen pressure on the surface of the alloy.

Comparing of oxidation kinetics by measurements of changes of thickness of oxidized layer with temperature and time, showed that oxidation rate is the highest for the alloy with the least amount of Cd and the lowest for the alloy with highest amount of Cd. At the same time, it can be concluded that at higher investigated temperatures (795°C) inner oxidation rate is higher. Hence, for applied synthesis conditions the temperature has the more significant influence on the process of inner oxidation.

Obtained experimental results of investigation of Ag-SnO<sub>2</sub> electrical contact materials with different

SnO<sub>2</sub> content and the influence of addition of small amount of In<sub>2</sub>O<sub>3</sub>, used to demonstrate (PM) production route, illustrate relation between synthesis conditions, microstructure, electrical and mechanical properties. By comparing of the obtained experimental it can be observed that sintering regime has the significant influence on the improvement of mechanical and electrical properties. It was found that the small addition of In<sub>2</sub>O<sub>3</sub> to Ag-SnO<sub>2</sub> has improved dispersion of main oxide SnO<sub>2</sub> in soft silver matrix and contributed to the activation of sintering process, hence caused foremost improvement of mechanical properties while keeping the good values of electrical conductivity. The same as for the samples without addition of In<sub>2</sub>O<sub>3</sub> the sintering regime in this case as well has the major influence on the improvement of functional properties.

The obtained values of hardness of the investigated Ag-CdO materials after applied IO regimes are in range 80 - 130 HV, while values of hardness of the investigated Ag-SnO<sub>2</sub> materials after applied PM regimes are in range 70.8 – 102 HV. Density of the IO Ag-CdO materials is in range 10.0 – 10.2 g/cm<sup>3</sup> whereas maximal values of density of the PM Ag-SnO<sub>2</sub> is obtained after sintering at 840°C for 2 hours.

Electrical conductivity of investigated Ag-CdO electrical contact material is in the range 45 – 52 MS/m and maximal value of the electrical conductivity of the investigated Ag-SnO<sub>2</sub> material is 38.5 MS/m.

It should be pointed out that the obtained microstructural characteristics and values of density, hardness and electrical conductivity of the both investigated electrical contact materials are comparable to each other and at the same time comparable to the same characteristics of the commercially available electrical contact materials.

Investigated process of making of electrical contacts by inner oxidation of Ag-Cd alloy allows getting complex forms of electrical contacts economically compared to many alternative CdO free contacts, particularly silver tin oxide (Ag-SnO<sub>2</sub>), that are much more difficult to fabricate because of poor metallurgical properties leading to low process yields and higher costs. However, the comparison of test results shows that the currently available Ag-SnO<sub>2</sub> materials have the potential to replace Ag-CdO without changing the design of the contactors, which is the one of the most important parameters from the application and economical point of view.

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## REFERENCES

- [1] Shen, Y. S.; Lattari, P.; Gardner, J.; Wiegard, H., ASM Handbook, Powder Metal Technologies and Applications, 1998, 7, 1025
- [2] Holm, R.; Electrical Contacts - Theory and applications, Springer, 4<sup>th</sup> Ed., 2000.
- [3] Braunović, M.; Myshkin, N.K.; Konchits, V.V., Electrical contacts – Fundamentals, Applications and Technology, CRC Press, Taylor and Francis Group, 2007.
- [4] Talijan, N.; Stajić-Trošić, J.; Čosović, V.; Grujić, A.; Romhanji, E., Electrical and mechanical properties of silver based electrical contact materials, 4<sup>th</sup> Balkan Conference on Metallurgy 27-29 Sept. 2006, Zlatibor (Serbia), Proceedings of, p.445.
- [5] Talijan, N.; Čosović, V.; Stajić-Trošić, J.; Grujić, A.; Živković, D.; Romhanji, E., J. Mining and Metallurgy, 2007, 43 B (2), 171
- [6] Talijan, N.; Stajić-Trošić, J.; Čosović, V.; Grujić, A.; Romhanji, E., 10<sup>th</sup> International Research/Expert Conference, Trends in Development of Machinery and Associated Technology, TMT 2006, Barcelona-Lloret de Mar, Spain, 2006, pp. 361-364
- [7] Slade, P.G., ed., Electrical Contacts: Principles and Applications, CRC Press, (1999), p.684.
- [8] Talijan, N.; Stajić-Trošić, J.; Čosović, V.; Grujić, A.; et al., Composite Ag-CdO electrical contacts made by inner oxidation, 6<sup>th</sup> International Power Systems Conference, Nov.2005, Timisoara (Romania), Proceedings, p.569.
- [9] Lorrain, N.; Chiffon, L.; Carry, C.; Delcroix, P.; Le Caër, G., Mat. Sci. Eng. A, 2004, 367, 1-8
- [10] Birks, N.; Meier, G.H.; Pettit, F.S.; Introduction To The High Temperature Oxidation of Metals, Cambridge University Press, New York, 2006
- [11] Wojtasik, K.; Missol, W., PM helps develop cadmium – free electrical contacts, Elsevier Ltd, 2004
- [12] Lungu, M.; Gavrilu, S.; Canta, T.; Lucaci, M.; Enescu, E.; J Optoelectron Adv M, 2006, 8, 576

## IZVOD

## ELEKTROKONTAKTNI MATERIJALI NA BAZI SREBRA

*Kompozitni elektrokontaktni materijali na bazi srebra i oksida različitih metala koriste se već dugi niz godina u različitim tipovima elektro uređaja za uspostavljanje i prekidanje električnog kola. Elektrokontaktni materijal tipa Ag-AgCdO je zahvaljujući izvanrednim električnim i mehaničkim karakteristikama u proteklom periodu široko primenjivan za mala i srednja strujna opterećenja. Međutim, zbog toksičnosti CdO, primena ovog tipa elektrokontaktnog materijala je morala da bude redukovana na minimum. Savremena istraživanja su dovela do realizacije novih ekoloških elektrokontaktnih materijala u kojima je CdO zamenjen manje štetnim metalnim oksidima, ali uz zadržavanje zahtevanih finalnih karakteristika. Istraživanja su pokazala da Ag-SnO<sub>2</sub> kompozitni materijal zadovoljava najveći broj zahtevanih svojstava u odnosu na konvencionalni Ag-CdO elektrokontaktni materijal. Rezultati eksperimentalnih istraživanja tehnoloških postupaka dobijanja različitih tipova elektrokontaktnih materijala na bazi srebra prikazani su u ovom radu kroz definisane tehnološke faze sa optimizovanim procesnim parametrima. Obrazložene su istražene i optimizovane metode dobijanja. Ispitane su i uporedo prikazane strukturne, mehaničke i električne karakteristike istraživanih i realizovanih tipova elektrokontaktnih materijala na bazi srebra. Ilustrovane su i konkretne vrste primene.*

**Ključne reči:** elektrokontakti, srebro-metalni oksidi, metode dobijanja, svojstva