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MICROSTRUCTURE AND PROPERTIES OF SILVER BASED CADMIUM FREE ELECTRICAL CONTACT MATERIALS

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Abstract

The presented work covers part of experimental results of simultaneous study of microstructure, density, hardness and electrical conductivity of sintered electrical contact materials based of Ag-SnO_2 with 8, 10 and 12 mass% SnO_2. The mentioned characteristics were analyzed in the function of different sintering regimes and after additional mechanical treatment (forging and rolling). The influence of small addition of In_2O_3 (2.9 mass%) on the increase of dispersion of main oxide SnO_2 in Ag matrix is observed and presented also.

Keywords: Ag-SnO_2, electrical contact materials, powder metallurgy, structure, mechanical properties, electrical conductivity

1. Introduction

Silver cadmium oxide electrical contact materials (Ag-CdO) have been used for many years for different low voltage devices of contactor type because of their excellent electrical and mechanical properties [1]. Based on the EU directive [2] 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 oxide dispersed in silver matrix, in order to obtain new ecological electrical contact materials. The new ecological electrical contact materials have

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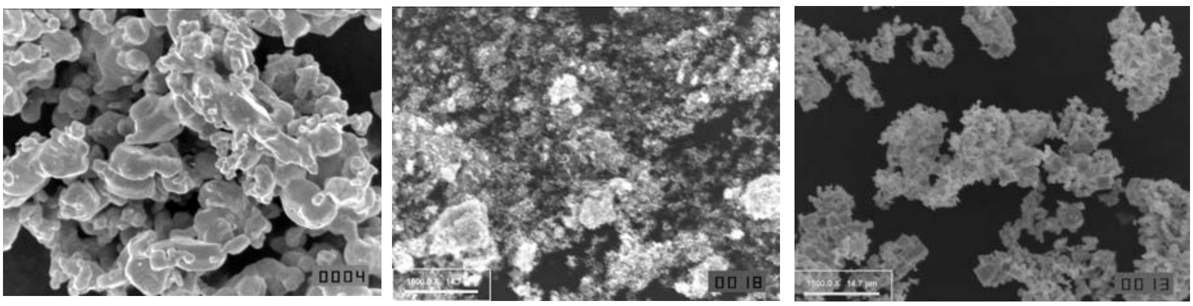
many advantages from the technical, economical and environmental point of view [3,4]. It was found that the Ag-SnO_2 materials have the most favorable properties [5]. Nowadays, it is known that electrical and mechanical properties of Ag-SnO_2 electrical contact materials can be improved by adding small amounts of In_2O_3, Bi_2O_3, CuO and WO3 [6,7]. These additives increase dispersion of main oxides (SnO_2) in silver matrix and to the activation of sintering process in order to gain optimal microstructure which results in improved electrical and mechanical properties. Like Ag-CdO contact materials, Ag-SnO_2 are mainly produced by powder metallurgy techniques [8] that provide optimal mictrostructure which results in improved mechanical and electrical properties.

2. Experimental

The influence of content of main oxide SnO_2 (8, 10, 12 mass%) and addition of In_2O_3 (2.9 mass%) on structural, mechanical and electrical characteristics of the Ag-SnO_2 electrical contact material was investigated. The studied electrical contact material based on Ag-SnO_2 with small addition of In_2O_3 was produced by powder metallurgy (PM) method from pure powders (Ag - 99.9%, SnO_2 - 99.9%, In2O3 - 99.99%). The silver powder used for investigations was obtained by chemical process and the SnO_2 and In_2O_3 powders are the commercial powders produced by Merck. The SEM images of the powders that were used in investigation are presented on Fig. 1a), b) and c).

The powders used in investigation was very fine - submicron particles, and they are presented as large agglomerated particles. Therefore the homogenization was done in several steps both wet and dry. Uniformity of the obtained mixtures was controlled with the use of scanning electron microscope (SEM). The samples were pressed into 80×20×5 mm plates by the hydraulic press with the pressure of 98 MPa in steel dye. 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. The samples were sintered in electro-resistive oven with programmable digital temperature controller with the accuracy $\pm 1^{o}$C in the air atmosphere. The applied sintering regimes are presented on Fig. 2. After sintering the samples were forged and hot rolled with the low degree of reduction to the final thickness of 2 mm.

The microstructure was observed on



a) (×1500) b) (×1500) c) (×1500)

Fig. 1. SEM images of the powders used in investigation a) Ag, b) SnO2, c) In_2O_3

polished and etched cross-sections of the samples using the metallographic light microscope Leica DM ILM. Density of the samples was determined by standard methods (ASTM B 311-93 (2002) e1).

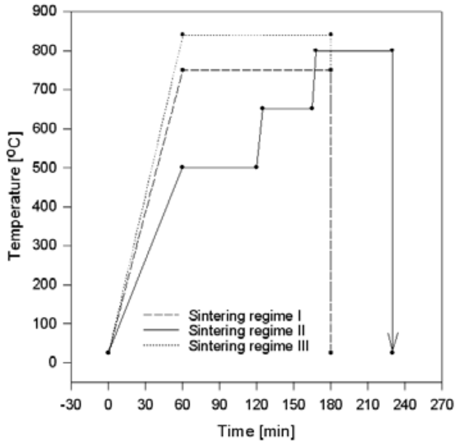


Fig. 2. Applied sintering regimes in sintering process of investigated Ag-SnO_2 and Ag-SnO_2 In_2O_3 electrical contact materials

Vickers hardness (applying load of 5 kp) was measured after the applied sintering and mechanical treatment regimes. Electrical conductivity of the investigated materials was measured using the Foerster SIGMATEST 2.069 eddy current instrument for measurements of electrical conductivity of non-ferromagnetic metals based on complex impedance of the measuring probe, with the 8 mm probe. Technological procedure of production of investigated materials by powder metallurgy method (PM) is presented on Fig. 3.

3. Results and Discussion

The SEM images of the Ag-SnO_2 (92:8) and Ag-SnO_2 In_2O_3 (87.8:9.30:2.90) mixtures that were used in investigation are presented on Fig. 4.

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_2 (92:8) electrical contact materials after the applied sintering regimes and additional mechanical treatment are shown on Fig. 5. The presented cross-sections are with and without Ag layer.

The obtained microstructures of the investigated Ag-SnO_2 In_2O_3 (87.8 : 9.30 : 2.90) electrical contact materials after different sintering regimes and mechanical treatment are presented on Fig. 6.

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. 5. and Fig. 6. it can be seen that the components SnO_2 and In_2O_3 are uniformly dispersed in silver matrix. Although, the Ag-SnO_2 92:8 (Fig. 5)

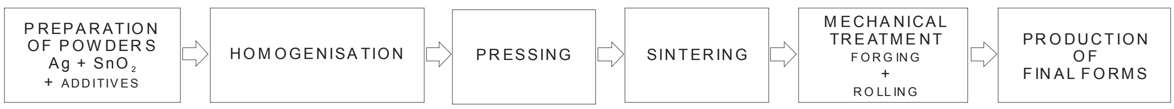
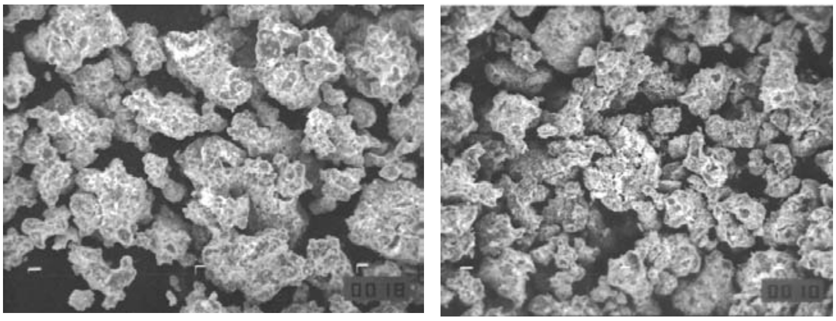


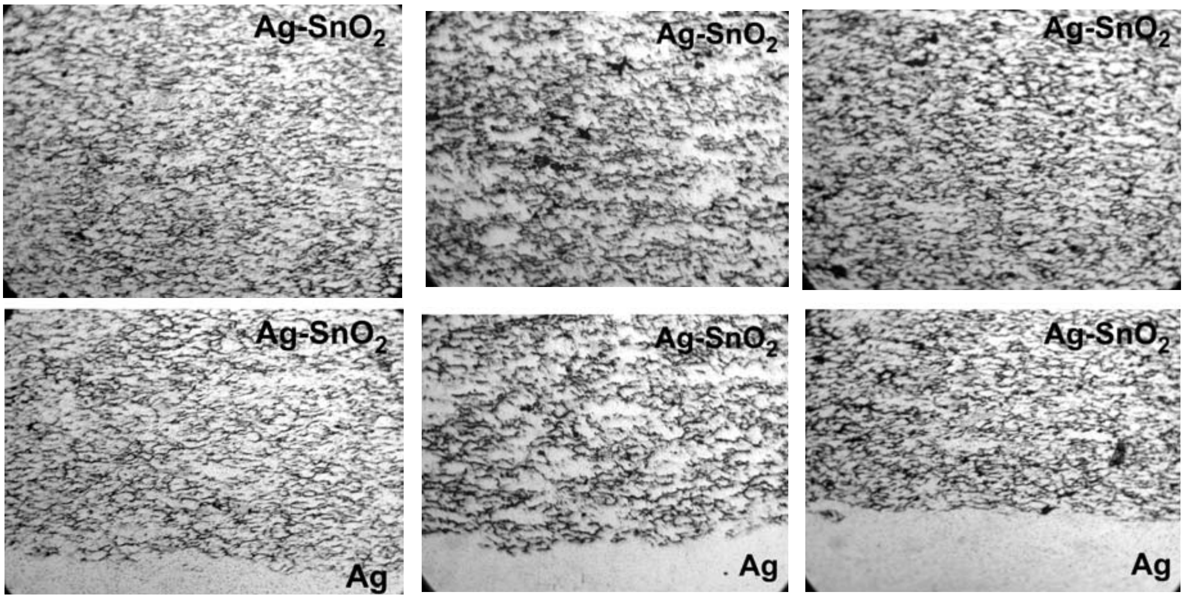
Fig. 3. Technological procedure of production of investigated Ag-SnO_2 electrical contact materials



a) b)

Fig. 4. SEM images (×500) of a) Ag-SnO_2, and b) Ag-SnO_2 In_2O_3 mixtures

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 SnO_2 in the "net" walls is evident for the sample sintered in multi stage sintering regime (Fig.5 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. Summarized experimental results of density, hardness and electrical conductivity measurements of investigated electrical contact materials in relation to sintering conditions and mechanical treatment regimes are presented in the Table 1.



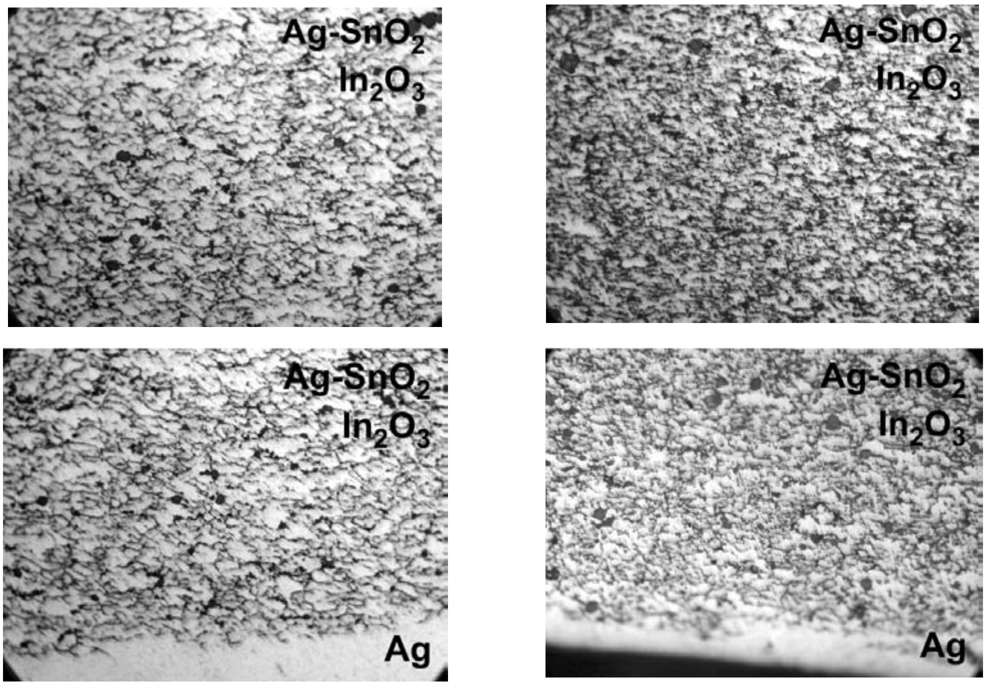
I II III

Fig. 5. Microstructure (cross-section) (×500) of Ag-SnO_2 (92:8) sintered at regimes I, II, III and additionally mechanically treated

Table 1. Mean values of density, hardness and electrical conductivity of investigated electrical contact materials with corresponding sintering conditions and mechanical treatment regimes

Sample No.	Ag [mass%]	SnO_2 [mass%]	In_2O_3 [mass%]	Sintering regime	Density [g/cm^3]	Hardness [HV/5kp]	Electrical Conductivity [MS/m]
1	88.0	12.00	–	I	7.2	73.2	26.98
2	90.0	10.00	–	I	7.9	73.6	33.32
3	92.0	8.00	–	I	7.4	70.8	35.75
4	92.0	8.00	–	II	9.6	91.6	36.04
5	92.0	8.00	–	III	9.8	102.0	38.57
6	87.8	9.30	2.90	I	9.0	77.2	27.13
7	87.8	9.30	2.90	II	9.4	84.2	30.75

The presented experimentally obtained results of microstructural analysis and determined mean values of density, hardness and electrical conductivity of the investigated Ag-SnO_2 and Ag-SnO_2 In_2O_3 electrical contact materials can be matched up to the mean values of the same characteristics of the Ag-CdO electrical contact materials [9,10]. Good results of density and hardness and consequently electrical conductivity were achieved for the Ag-SnO_2 with addition of In_2O_3



I II

Fig. 6. Microstructure (cross-section) (×500) of Ag-SnO_2 In_2O_3 (87.8: 9.30: 2.90) after sintering at regimes I, II and additional mechanical treatment

(2.9 mass%) also. This is completely understandable, since the small amounts of In_2O_3 (or other additives like Bi_2O_3, CuO and WO_3) will increase dispersion of main oxide in silver matrix and the activation of sintering process [4,6]. This way the optimal microstructure can be obtained which would result in improvement of electrical and mechanical characteristics.

6. Conclusion

Maximal values of density, hardness and electrical conductivity of the Ag-SnO_2 electrical contact material with 8 mass% of SnO_2 were obtained after sintering of the material at 840^oC for 2 hours and additional mechanical treatment. By comparing of the obtained experimental results of investigation of Ag-SnO_2 electrical contact materials with different SnO_2 content, it can be observed that sintering regime has the significant influence on the improvement of mechanical and electrical properties. It was experimentally confirmed that the small addition of In_2O_3 to Ag-SnO_2 has caused foremost improvement of mechanical properties while keeping the good values of electrical conductivity. Obtained microstructure characteristics and values of density, hardness and electrical conductivity of the investigated Ag-SnO_2 and Ag-SnO_2 In_2O_3 electrical contact materials are comparable to the same characteristics of the electrical contact materials based on Ag-CdO.

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References

1. N. Talijan, J. Stajić-Trošić, V. Ćosović, A. Grujić, E. Romhanji, Composite Electrical Contacts Based on Silver, 10th International Research/Expert Conference, Trends in Development of Machinery and Associated Technology, TMT 2006, Barcelona-Lloret de Mar, Spain, 2006.
2. EU Directive 2002/95/EC, *Official Journal of the European Union*, L37/19, 2003
3. N. Talijan, J. Stajić-Trošić, V. Ćosović, A. Grujić, E. Romhanji, Electrical and mechanical properties of silver based electrical contact materials, 4th Balkan Conference on Metallurgy, Zlatibor, Serbia, 2006.
4. K. Wojtasik, W. Missol, PM helps develop cadmium - free electrical contacts, Elsevier Ltd, 2004
5. O. Nilsson, F. Hauner, D. Jeannot, Proc. of the 50-th IEEE Holm Conf. on El. Contacts and the 22-nd Int Conf. On El. Contacts, 2004, p. 70
6. M. Lungu, S. Gavriliu, T. Canta, M. Lucaci, E. Enescu, *Journal of optoelectronics and advanced materials*, 8 (2006) 576-581
7. C. Leung, E. Streicher, Proc. of the 48-th IEEE Holm Conf. on El. Contacts, 2002, p.21
8. W. Weise, R. Wolmer, P. Braumann, US Patent, 5798468 (1998)
9. Technical Documentation - METALOR
10. Technical Documentation - AMI DODUCO