19h International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2015, Barcelona, Spain 22-23 July 2015

IMPROVEMENT OF OXIDE DISPERSION IN Ag-SnO_2 AND Ag-ZnO ELECTRICAL CONTACT MATERIALS USING TEMPLATE METHOD OF PREPARATION

Vladan R. Ćosović,
University of Belgrade,
Institute of Chemistry, Technology and Metallurgy,
Njegoševa 12, 11000 Belgrade,
Serbia

Aleksandar R. Ćosović
Institute for Technology of Nuclear and other Raw Materials,
Franše d' Eperea 86, 11000 Belgrade,
Serbia

Dragana T. Živković
University of Belgrade, Technical Faculty Bor,
V.J. 12, 19210 Bor,
Serbia

Duško Minić
University of Priština, Faculty of Technical Sciences,
Knjaza Miloša 7, 38220 Kosovska Mitrovica,
Serbia

Ana I. Kostov
Institute for Mining and Metallurgy Bor,
Zeleni bulevar 35, 19210 Bor,
Serbia

Nadežda M. Talijan
University of Belgrade,
Institute of Chemistry, Technology and Metallurgy,
Njegoševa 12, 11000 Belgrade,
Serbia

ABSTRACT
In the present study, an innovative attempt has been made to increase dispersion of Ag-SnO_2 and Ag-ZnO contact materials by introducing respective metal oxide nanoparticles in silver matrix and preparation of nanocomposite powders by template method using soluble starch as template material. Density and porosity of the investigated materials were determined by standard methods, while further characterization was carried out using scanning electron microscopy (SEM), Vickers hardness and eddy current conductivity measurements. It was found that the samples prepared by template method, exhibit finer dispersion of oxides, higher hardness, higher density and lower porosity, compared to their microparticle counterparts prepared by conventional powder mixing, and have electrical conductivity comparable with those of commercial contact materials.
Keywords: Silver/metal oxide contacts, template method, physical properties

1. INTRODUCTION
Silver based electrical contact materials are widely used and industrially important group of functional materials [1]. Since use of generally superior Ag-CdO contacts is limited due to EU environmental legislations (RoHS, WEEE), in recent years, a lot of attention has been dedicated to Ag-SnO_2 and Ag-ZnO materials as promising, more environmentally friendly substitutes. Still, over-temperature behavior and workability of these materials is regarded as rather poor when they are produced by common processing routes [2]. Hence, various attempts have been made to improve their performance and applicability. The overall research approach is based on generally accepted view that smaller metal oxide particles contribute to formation of anti-welding characteristics and under certain

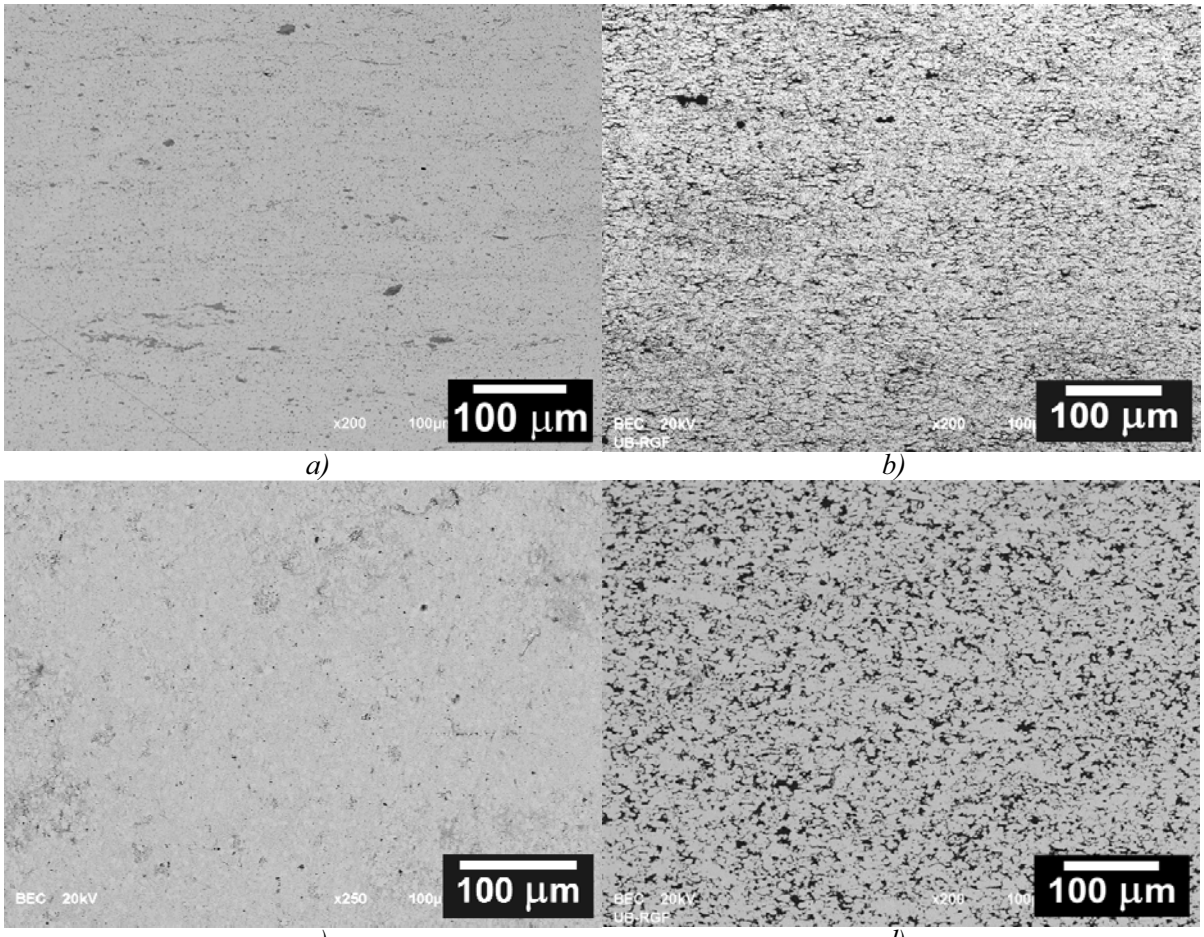
conditions decrease erosion rate of the electrical contact [3]. Also, in order to improve the anti-welding behavior, hardness and wear resistance of contact materials it is necessary to obtain uniform dispersion of metal oxide particles in a soft silver matrix [3,4]. Given that such fine microstructures cannot be obtained by conventional mixing of powders [4], in the present study, template method [5] has been applied for introduction of SnO_2 and ZnO nanoparticles in silver matrix and preparation of composite powders in order to produce Ag-SnO_2 and Ag-ZnO contact materials with increased dispersion. Microstructure and physical properties of the obtained silver-nanoparticle metal oxide composites such as density, porosity, hardness and electrical conductivity are discussed and presented in comparison to their micro particle counterparts prepared by conventional mixing route.

2. EXPERIMENTAL

Commercial SnO_2 and ZnO (40-100 nm) nanoparticles as well as $AgNO_3$ powder produced by Sigma-Aldrich were used as precursors and soluble starch as a soft template for synthesis of Ag-SnO_2 and Ag-ZnO composite powders via template method. The applied synthesis route utilizes the fact that $AgNO_3$, when heated, thermally decomposes to elemental Ag instead of corresponding oxide. In the first step separate water solutions of soluble starch and $AgNO_3$ were prepared along with separate SnO_2 and ZnO nanoparticle suspensions. The prepared nanoparticle suspensions were then slowly added to respective starch solutions during vigorous mixing. After few minutes $AgNO_3$ water solution was slowly added to the mixtures. Both $AgNO_3$ and MeO nanoparticles (Me=Sn, Zn) were added in quantities necessary to achieve desired (92:8) Ag:MeO weight ratio in final material. The prepared mixtures were then dried at 80^{o}C in chamber dryer until water was evaporated and solid composites were obtained. The solid composites were subsequently burned and put into a muffle furnace pre-heated at 650^{o}C and calcinated for 4h. During the combustion and later calcination, silver nitrate was transformed to elemental Ag with embedded SnO_2 and ZnO nanoparticles, respectively and the starch template was removed. The samples of microparticle Ag-MeO (92:8) materials were prepared by conventional mixing of pure Ag powder, produced by chemical precipitation synthesis route, and very fine commercial SnO_2 and (ZnO - 99.9%) submicron particle powders. Comprehensive characterization of the starting powders is given in [6]. Both wet and dry homogenization of the powder mixture was carried out. All final Ag-MeO contact materials were prepared via conventional powder metallurgy route [7]. The obtained composite powders and microparticle powder mixtures were cold pressed into blocks with dimensions 25.4×11×3 mm, by applying pressure of 360 MPa. The obtained green compacts were then sintered for 3h at 820^{o}C in the air atmosphere and subsequently forged at 800^{o}C with the low degree of reduction. The obtained samples were then annealed at 750^{o}C for 30 min and quenched in water. Microstructures of the prepared contact materials were studied on polished cross-section surfaces using JEOL JSM 6610LV scanning electron microscope (SEM). Density and porosity of the obtained samples were determined by standard methods described in more detail in [6]. Hardness measurements were carried out on polished samples at room temperature using a Vickers hardness tester applying load of 5 kp. The reported hardness values are an average of five readings. Electrical conductivity of the investigated materials was measured using Foerster SIGMATEST 2.069 eddy current instrument with the 8 mm diameter probe.

3. RESULTS AND DISCUSSION

Microstructures of the studied Ag-MeO electrical contacts after sintering, mechanical treatment and subsequent annealing are illustrated by SEM metallographic images of polished cross-sections presented in Figure 1. The presented images demonstrate high uniformity of the obtained materials as well as notable differences in homogeneity between individual samples. From Figure 1a and Figure 1c it is evident that the samples prepared by template method have significantly higher MeO particle dispersion whereas the samples prepared by conventional route (Figure 1b, Figure 1d) appear to be less fine and more porous with MeO particles predominantly situated on silver grain boundaries. The observed differences in microstructure will most certainly affect structure dependent properties of the prepared Ag-MeO electrical contacts. For that reason important physical properties of the studied silver-metal oxide electrical contact materials such as density, hardness and electrical conductivity were measured after final stages of processing at room temperature. An overview of the determined physical properties is given in Table 1.



a) *b)*

c) *d)*

Figure 1 - SEM images of microstructures of the studied electrical contacts prepared by: a) Ag-SnO_2 template method, b) Ag-SnO_2 conventional mixing of powders c) Ag-ZnO template method, d) Ag-ZnO conventional mixing of powders

Table 1. Comparative presentation of physical properties of the prepared electrical contact materials

Preparation method	**Composition**	**Density** [g/cm^3]	**Hardness** [HV5]	**Conductivity**	
				[MS/m]	[%IACS]
Template method / powder metallurgy	Ag-SnO_2 (92:8) nano	9.86	123	38.92	67
Conventional mixing / powder metallurgy	Ag-SnO_2 (92:8) micro	9.53	87	44.75	77
Template method / powder metallurgy	Ag-ZnO (92:8) nano	9.55	96	35.27	61
Conventional mixing / powder metallurgy	Ag-ZnO (92:8)	9.49	82	38.65	67

From Table 1 it can be seen that Ag-SnO_2 and Ag-ZnO materials prepared via template method exhibit higher values of density and hardness compared to conventionally prepared microparticle ones. In line with the observed microstructures (Figure 1), it can be assumed that this is the result of finer and more homogenous microstructures that enabled greater dispersion hardening. Such improved properties are desired from the application point of view in terms of better wear resistance and longer exploitation life. In contrast, higher values of electrical conductivity of the microparticle Ag-SnO_2 and Ag-ZnO materials can be ascribed to the less uniform microstructures and presence of oxide free zones that provide better connectivity of the silver grains, as it can be seen on Figure 1b and Figure 1d. Somewhat lower conductivity of the materials prepared via template method is

expected given that electrical conductivity generally decreases with reduction of metal oxide particle size and increase of their dispersion due to changes in mean free path of conduction electrons [3]. Nevertheless, the measured values of electrical conductivity (Table 1.) are is still in the required range for commercial electrical contacts of this type.

4. CONCLUSION

An attempt has been made to improve dispersion of metal oxide particles in Ag-MeO (Me = Sn, Zn) contact materials by using template method. Structure and physical properties of the obtained silver-nanoparticle metal oxide composites are discussed and presented in comparison to their microparticle metal oxide counterparts. The obtained results illustrate significant influence of the applied preparation method on microstructure and structure dependent properties as the results of microstructural analysis confirm that higher dispersion was obtained by introduction of MeO nanoparticles by template method than for conventionally prepared microparticle materials. Consequently, higher values of hardness, density and lower porosity were obtained which is very important from the application point of view. In line with that, the observed enhancement of hardness was attributed to greater dispersion hardening. Despite small decrease, the measured values of electrical conductivity were still retained on the normal level for this type of electrical contacts. As the physical, mechanical and electrical properties of the contact materials prepared by template method are comparable to Ag-CdO and are within the required range of values for commercial electrical contact materials of the same composition, it can be concluded that the template method can be successfully used in production of Ag-MeO contact materials.

5. ACKNOWLEDGEMENT

This work has been supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects OI 172037 and TR 34023).

6. REFERENCES

[1] Braunović M., Myshkin N.K., Konchits V.V.: Electrical contacts – Fundamentals, Applications and Technology, CRC Press, Taylor and Francis Group, Boca Raton, 2007.
[2] Zheng Ji, Songlin LI, Fyqi DOU, Tonghui LI: Preparation and microstructure characterization of a nano-sized Ti4+-doped AgSnO2 electrical contact material, Rare Metals, 28(1) (2009) 19-23.
[3] Heringhaus F., Braumann P., Ruhlicke D., Susnik E., Wolmer R.: On the Dispersion in Ag-SnO2 based Contact Materials, Proc. 20th Int. Conf. on Electr. Contact Phenom. Stockholm, 2000., 199-204.
[4] Wolmer R., Mueller M., Ruehlicke D., Goia D.; US patent Pub. No.: US 2001/0051102 A1
[5] Ćosović V.R., Ćosović A.R., Živković D.T., Kostov A.I., Talijan N.M.: The Influence of SnO2 Nanoparticles and Method of their Introduction on Microstructure and Properties of Ag-SnO2 Electrical Contacts, 16th International Research/Expert Conference ”Trends in the Development of Machinery and Associated Technology” TMT 2012, Dubai, AUE, 2012., 147-150.
[6] Ćosović V., Talijan N., Živković D., Minić D., Živković Ž.: Comparison of properties of silver-metal oxide electrical contact materials, J. Min. Metall. Sect. B-Metall. 48 (1) B (2012) 131-141.
[7] Ivanović A.T., Milojević S.F., Marjanović V.M., Madić B.N.: Production the high electric conductive materials for contacts based on silver by the use of sintermetallurgical method, 15th International Research/Expert Conference ”Trends in the Development of Machinery and Associated Technology” TMT 2011, Prague, Czech Republic, 2011., 685-688.