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Microstructure Refinement and Physical Properties of Ag-SnO_2 Based Contact Materials Prepared by High-Energy Ball Milling

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Abstract:

High energy ball milling was used in order to improve dispersion of metal oxide in Ag-SnO_2 electrical contact materials. The processed Ag-SnO_2 (92:8) and Ag-$SnO_2In_2O_3$ (87.8:9.30:2.9) powder mixtures were subsequently consolidated to bulk solid pieces by conventional powder metallurgy method. The characterization of the prepared samples included microstructural analysis by XRD and SEM, as well as measurements of physical properties such as density, hardness and electrical conductivity. The results of X-Ray analysis point to reduction of crystallite size after milling of about ten times. Microstructures of sintered Ag-SnO_2 and Ag-SnO_2 In_2O_3 materials display very fine dispersion of the oxide components in silver matrix. Somewhat higher uniformity was obtained for Ag-SnO_2 In_2O_3 material which was illustrated by results of SEM analysis and more consistent microhardness values. The obtained values of studied physical properties were found to be in accordance with observed higher dispersion of metal oxide particles and comparable to properties of commercial electrical contact materials of this type.

Keywords: *Silver-metal oxide electrical contacts, High-energy ball milling, powder metallurgy, Microstructure, Physical properties.*

1. Introduction

Silver-metal oxide composites are extensively used for many electrical contact applications [1]. Accordingly, numerous formulations and synthesis methods have been developed. As each of them is characterized by certain benefits, limitations and disadvantages, selection of the particular material or production method usually represents a compromise between required functional properties, economy and environmental legislation [2].

As a promising, more environmentally friendly replacement for traditional Ag-CdO contact materials, Ag-SnO_2 contacts are industrially important group of materials [3,4].

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However, when produced by traditional manufacturing methods they are characterized by rather poor over-temperature behavior and poor workability [5]. Considering that these important materials properties are found to be structure dependent, the common approach for improvement of performance of Ag-SnO_2 contacts is increase of the dispersion of metal oxide particles by applying specific synthesis conditions and/or synthesis route.

One of the alternative processes for improvement of homogeneity is high energy ball milling or mechanical alloying. During the high-energy ball milling process highly accelerated grinding balls continuously collide with a mill chamber walls and each other thus causing mixing, deformation, grinding, welding, fracture and re-welding of the milled material caught in between, hence creating very homogenous distribution of particles. Although, the resulting powders are characterized by high dispersion they have tendency to exhibit significant inactivity during sintering [6].

It is widely known that the functional properties of the Ag-SnO_2 electrical contact materials can be improved by addition of different metal oxide components. It was found that small addition of metal oxides such as In_2O_3, Bi_2O_3, CuO or WO_3 increase dispersion of main oxides (SnO_2) in silver matrix and contribute to the activation of sintering process [7,8].

In the present study, Ag-SnO_2 and Ag-$SnO_2In_2O_3$ powder mixtures were processed by high-energy ball milling and subsequently consolidated to bulk solid pieces by conventional powder metallurgy method. The obtained electrical contact materials were then evaluated in terms of their microstructure and physical properties.

In the present study, Ag-SnO_2 and Ag-$SnO_2In_2O_3$ composite powders were processed by high-energy ball milling and subsequently consolidated to bulk solid pieces by conventional powder metallurgy method. The obtained electrical contact materials were then evaluated in terms of their physical properties.

2. Experimental

The studied Ag-SnO_2 and Ag-$SnO_2In_2O_3$ contact materials were prepared using pure silver powder produced by aqueous precipitation from silver nitrate as well as commercial SnO_2 and In_2O_3 powders produced by Sigma-Aldrich. Particle size of the starting silver powder was determined by laser diffractometry using Malvern Instruments Mastersizer 2000 laser diffractometer with the Scirocco 2000 module. The obtained particle size distribution curve is given in Fig. 1.

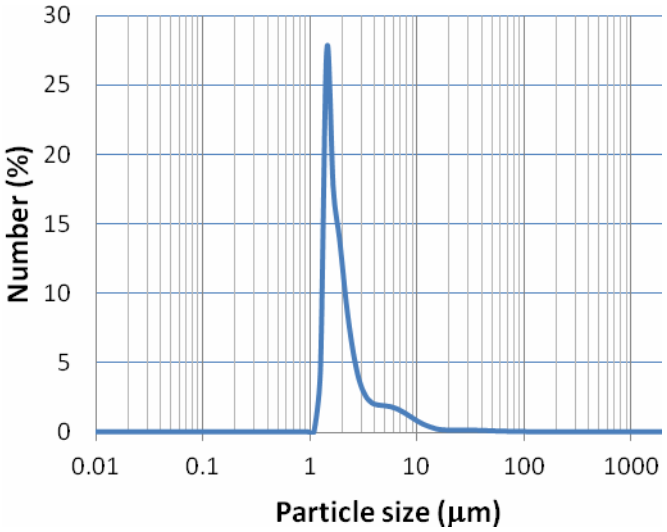


Fig. 1. Particle size distribution curve of the obtained silver powder.

The presented curve (Fig. 1.) demonstrates rather narrow size distribution of the obtained Ag particles with the mean particle size having following values: d(0.1) = 1.299 μm, d(0.5) = 1.666 μm and d(0.9) = 4.605 μm.

For the purpose of this study, the Ag-SnO_2 samples were prepared with the 92:8 weight ratio of Ag:SnO_2 and the Ag-$SnO_2In_2O_3$ samples with the 87.8:9.30:2.9 weight ratio of Ag:SnO_2:In_2O_3.

The starting powder blends were mixed and milled in the Fritsch Pulverisette 7 high speed planetary mill at 600 rpm for 3h with 20:1 ball to powder ratio using the 5 mm tungsten carbide balls as grinding bodies.

X-ray powder diffraction experiments were conducted on Philips PW1710 X-Ray diffractometer using Cu Kα radiation. Data for the Rietveld refinement were collected between 20 and 100° 2θ. Counting time for the starting powder mixtures was 2.0 s per 0.025° 2θ step for prepared samples and 10 s per 0.100° 2θ step for the milled powders. The X-ray line-broadenings and phase composition (the Rietveld refinement) were analyzed by Fullprof software [9]. Crystallographic data for the identified phases present in the studied Ag-SnO_2 and Ag-$SnO_2In_2O_3$ powder samples are given in Tab. I.

Tab. I Crystallographic data for the phases present in the studied samples.

Chemical composition	Space group	Unit cell parameters	ICCD PDF No.
Ag	$Fm\bar{3}m$ (225)	a = 4.0861 Å	65-2871
SnO_2	$P4_2/mnm$ (136)	a = 4.7382; c = 3.1871 Å	41-1445
In_2O_3	$Ia\bar{3}$ (206)	a = 10.118 Å	6-0416

The subsequent consolidation of the obtained composite powders was carried out by conventional powder metallurgy route. The composite powders were firstly pressed in a steel die into Ø16 × 3 mm Tab.ts under pressure of 100 MPa. In a succeeding step of the process the green compacts were sintered for 2h at 820°C in a conventional air atmosphere electro-resistive furnace. In order to improve the density of the samples the obtained bulk solid pieces undergone multi-stage forging at 800°C with the low degree of reduction to the final thickness of 2 mm, followed by annealing at 750°C for 30 min and quenching in water.

Further characterization of the obtained Ag-SnO_2 and Ag-$SnO_2In_2O_3$ electrical contact materials i.e. evaluation of their physical properties was carried out after final stages of processing at room temperature. Microstructural analysis was carried out using JEOL JSM-6610LV scanning electron microscope (SEM). Density of the samples was determined by conventional method. Vickers hardness was determined using conventional tester with load of 5 kgf (kp). The reported hardness values are an average of five readings. For the microindentation hardness testing DHV-1000 Digital Micro Vickers Hardness tester was used and the measurements were made at indentation load of 0.245 N and loading time of 10s. 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

Since the studied silver-metal oxide composites represent in fact ductile-brittle system they follow characteristic mechanism of the microstructure refinement. In the course of high-energy ball milling process brittle material like SnO_2 undergoes grinding and fragmentation into progressively smaller particles to the point where stress induced by collision of the grinding balls is not sufficiently higher than the newly formed particle's fracture strength to cause its further fragmentation [10]. On the other hand, ductile silver phase deforms, flattens

into plates and fractures. At the same time, both materials are mixed and joined together by cold-welding process into composite particles that successively undergo fracturing and re-welding with random orientation thus creating very fine dispersion of the oxide particles in silver matrix.

The final Rietveld plots (with respective phases present) of the Ag-SnO_2 and Ag-$SnO_2In_2O_3$ of the starting powder blends and composite powders obtained after high energy ball milling are shown in Fig. 2. Generally speaking, all the peaks can be ascribed to the face-centered cubic structure of silver and SnO_2, and In_2O_3 in the latter two samples. Considering that the presented XRD profiles show diffraction peaks corresponding to starting powders as well as high thermal stability of SnO_2 and In_2O_3, it can be safely assumed that during milling of Ag-SnO_2 and Ag-$SnO_2In_2O_3$ mixtures, silver powder and metal oxide powders do not chemically react with each other.

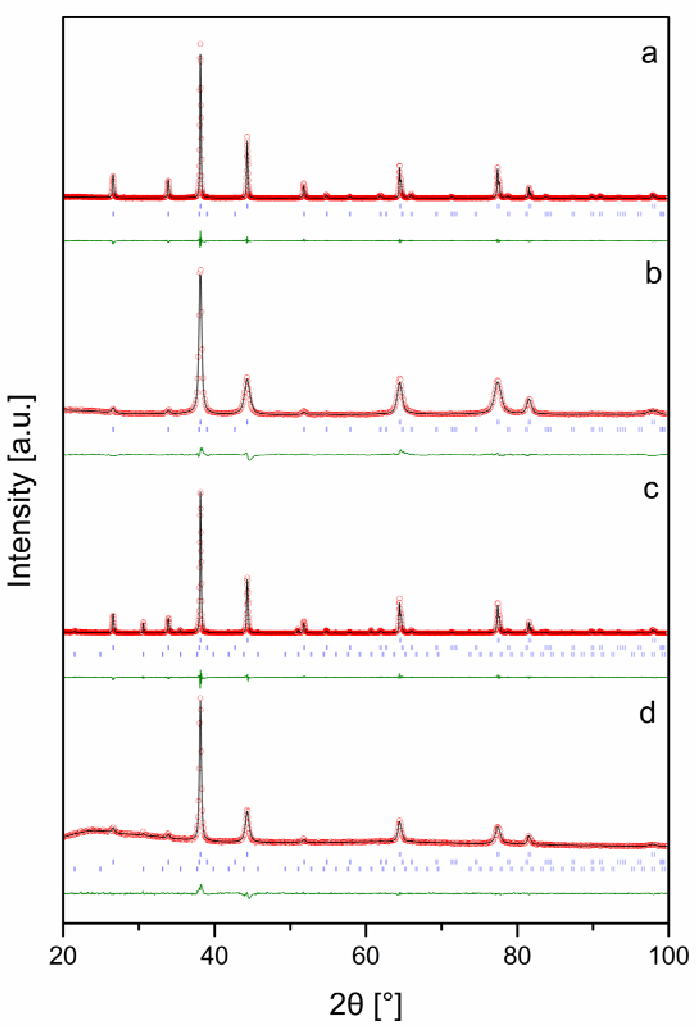


Fig. 2. X-Ray diffractograms of the: a) starting Ag-SnO_2 mixture; b) composite Ag-SnO_2 powder prepared by high energy ball milling technique; c) starting Ag-$SnO_2In_2O_3$ mixture and d) composite Ag-SnO_2 powder prepared by high energy ball milling technique.

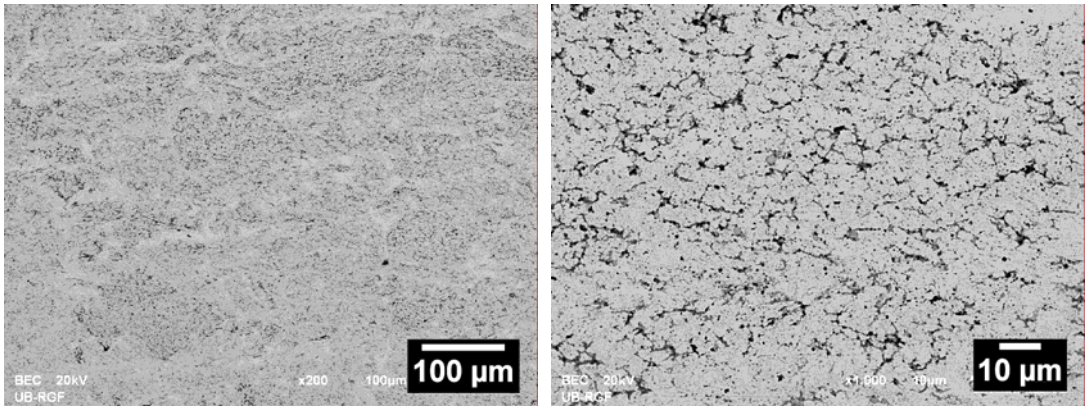
The Rietveld method was used for determination of phase composition and microstructural parameters of the silver phase. The obtained results are presented in Tab. II whereas final Rietveld refinement plots are given in Fig. 2.

Tab. II The selected results of Rietveld analysis of the studied powders (microstructural parameters and results of quantitative analysis).

Powder	Microstructural parameters of the Ag phase		Phase content (wt.%)		
	Crystallite size (Å)	Strain ($\times 10^{-3}$)	Ag	SnO_2	In_2O_3
Ag-SnO_2_a	1724	3	72(1)	28(1)	-
Ag-SnO_2_b	152	30	93(2)	7(1)	-
Ag-$SnO_2In_2O_3$_c	1722	4	72(1)	22(1)	6(1)
Ag-$SnO_2In_2O_3$_d	222	13	88(1)	9(1)	3(1)

The refined parameters of the unit cells of the present phases in a statistical sense do not deviate from the literature data. The presented results in Tab. II point to significant refinement of the microstructure as the crystallite size of the milled powders is almost ten times smaller than that of starting powder mixtures. In addition, the substantial increase of the strain can be observed for the milled powder samples. This is expected considering the scale of stress the powder mixtures (particles) are subjected to during the high energy ball milling process. The noticeable difference in phase composition of the starting and milled powders can be most certainly ascribed to the fact that degree of uniformity of the powder mixtures obtained by ball milling process cannot be achieved by conventional mechanical mixing of the starting powders. The important thing is that the desired silver to metal oxide ratio was obtained in the final composite powders.

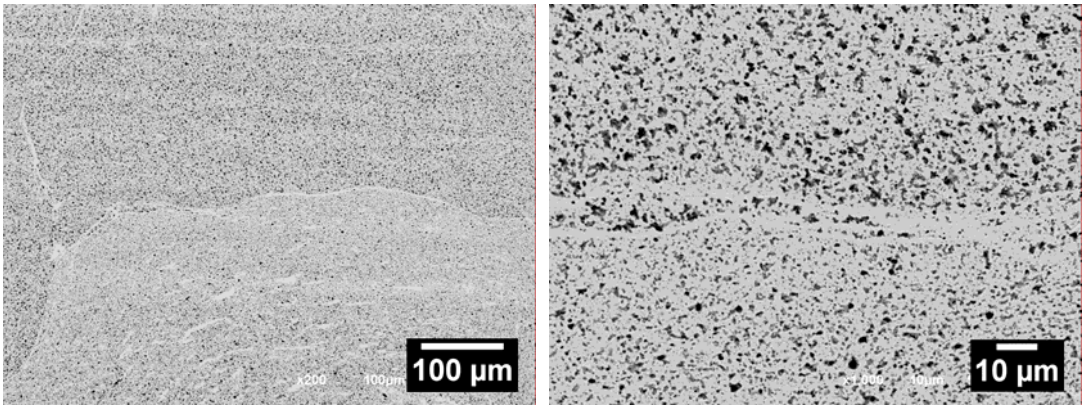
Microstructure of the Ag-SnO_2 and Ag-$SnO_2In_2O_3$ electrical contact materials obtained by further processing of the composite powders via powder metallurgy route is illustrated by the corresponding SEM images of the polished cross-sections given in Fig. 3. and Fig. 4., respectively. Both Ag-SnO_2 and Ag-$SnO_2In_2O_3$ materials after consolidation and sintering display very fine dispersion of the oxide component in silver matrix.



a) b)

Fig. 3. Microstructure of the obtained Ag-SnO_2 electrical contact material.

However, although obtained composite powders exhibit very homogenous microstructure, during subsequent pressing and sintering, due to poor wettability of the SnO_2 particles by the silver melt and their high thermal stability pure silver segregates on the composite particle surface. Consequently, in the microstructure of the final contact material (Fig. 3b), pure silver (oxide-free) regions can be observed which inevitably affect all structure dependent properties. The issue is commonly suppressed by introduction of small quantities of different additives such as In_2O_3, WO_3 and MoO_3 [11] and as it can be seen on Fig. 4., in case of Ag-$SnO_2In_2O_3$ material the oxide-free regions are much less pronounced and are in the form of thin silver lines.



a) b)

Fig. 4. Microstructure of the obtained Ag-$SnO_2In_2O_3$ electrical contact material.

Further characterization of the obtained Ag-SnO_2 and Ag-$SnO_2In_2O_3$ contact materials included microhardness testing which provided additional information regarding structure and physical properties. Optical micrographs of Vickers indentations into polished sample surfaces are given in Fig. 5.

a) b) c)

Fig. 5. Microphotographs of indentations on studied electrical contact materials: a) Ag-SnO_2 (79Hv25), b) Ag-SnO_2 (90Hv25) and c) Ag-$SnO_2In_2O_3$ (88Hv25).

Considering the observed differences in microstructure between the studied materials, for the Ag-SnO_2 material indentations were made both in silver matrix dominated (Fig. 5a) and in heterogeneous (Fig. 5b) regions. In terms of microhardness values, hardness of the silver matrix dominated region (Fig. 5a) is lower compared to the rest of the material. Existence of such regions most certainly lowers the overall bulk hardness of the material and thus its resistance to contact wear. On the other hand, more consistent microhardness values obtained for the Ag-$SnO_2In_2O_3$ sample support microstructural observations and confirm more homogenous microstructure.

Important physical properties of the prepared silver-metal oxide electrical contact materials are given in Tab. III.

Tab. III Physical properties of the prepared silver-metal oxide electrical contact materials.

Composition	Density [g/cm^3]	Hardness [HV5]	Conductivity [MS/m]	[%IACS]
Ag-SnO_2 (92:8)	9.48	84	39.80	69
Ag-$SnO_2In_2O_3$ (87.8:9.30:2.9)	9.55	89	32.54	56

From Tab. III it is evident that density of both Ag-SnO_2 and Ag-$SnO_2In_2O_3$ samples is below that for commercial materials. This is expected given that the applied consolidation process does not provide high density levels as the hot extrusion process typically used in

industry [12].

Considering that the Ag-$SnO_2In_2O_3$ sample generally exhibits higher homogeneity i.e. much finer and less abundant oxide free regions the observed higher hardness can be ascribed to better dispersion hardening of the silver matrix by dispersed metal oxide particles.

Measured values of electrical conductivity are in line with the composition of the samples and observed structural differences. As the Ag-SnO_2 sample contains more silver 92 wt.% its higher electrical conductivity is anticipated, in addition the observed silver matrix dominated - oxide free regions most certainly contribute to better connectivity of silver grains and thus higher overall conductivity. The lower electrical conductivity of the Ag-$SnO_2In_2O_3$ sample can be attributed to higher metal oxide content and higher homogeneity as well as possible reduction of the mean free path of conduction electrons. Nevertheless, the obtained values of the electrical conductivity for both samples are still comparable to conductivities of the most of commercially available electrical contact materials of the same type.

4. Conclusion

Microstructure and physical properties of the Ag-SnO_2 and Ag-$SnO_2In_2O_3$ electrical contact materials produced by combined high-energy ball milling and conventional powder metallurgy were studied. The results of Rietveld analysis applied on the obtained XRD profiles demonstrated significant refinement of microstructure with reduction of crystallite size after milling of about ten times. Microstructural analysis of both Ag-SnO_2 and Ag-$SnO_2In_2O_3$ materials after consolidation and sintering has revealed very uniform microstructure with high dispersion of the metal oxides in silver matrix. The presence of pure silver zones which were observed in the microstructure of the final contact materials was found to have effect on the structure dependent properties, particularly on increase of electrical conductivity and slight reduction of hardness values. The higher uniformity of Ag-$SnO_2In_2O_3$ material confirmed by obtained SEM micrographs and more consistent microhardness values was associated with addition of In_2O_3. The obtained values of density, hardness and electrical conductivity were found to be in line with observed higher dispersion of metal oxide particles and comparable with properties of commercial electrical contact materials of this type.

Acknowledgement

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Садржај: *Метода високоенергетског механичког млевења је примењена за припрему електроконтактних материјала на бази Ag-SnO_2 са циљем постизања високог степена дисперзије честица металних оксида у сребрној матрици. Смеше прахова састава Ag-SnO_2 (92:8) и Ag-$SnO_2In_2O_3$ (87.8:9.30:2.9) су после млевења процесуиране конвенционалним техникама металургије праха. Карактеризација синтерованих узорака обухватила је микроструктурну анализу (XRD, SEM) као и мерење важнијих физичких својстава: густина, тврдоћа и електрична проводљивост. Резултати XRD анализе су показали значајно смањење величине кристалита од око десет пута. Микроструктурна анализа синтерованих материјала указала је на веома фину и униформну дисперзију оксидних компоненти у сребрној матрици. SEM микрофотографије такође показују већу униформност микроструктуре узорка Ag-$SnO_2In_2O_3$ што потврђују и уједначеније вредности микротврдоће добијене за овај материјал. Измерене вредности анализираних физичких својстава су у сагласности са постигнутим већим степеном дисперзије честица металних оксида у сребрној матрици и упоредиве су са својствима комерцијалних електроконтактних материјала овог типа.*

Кључне речи *сребро-метал оксидни електрични контакти, млевење у високо-енергетском млину, металургија праха, микроструктура, физичка својства*