PROCESSING AND PROPERTIES OF SILVER-METAL OXIDE ELECTRICAL CONTACT MATERIALS

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Abstract
The presented study gives a brief overview of the experimental results of investigations of different production technologies of silver-metal oxide electrical contact materials in relation: processing method - properties. The two most common routes of production, i.e. internal oxidation/ingot metallurgy and powder metallurgy are demonstrated on the example of Ag-CdO and Ag-ZnO materials. For illustration of alternative processing routes that provide higher dispersion of metal-oxide particles in silver matrix more environmentally friendly Ag-SnO₂ contact materials are used. Processing of electrical contact materials by mechanical mixing of starting powders in high energy ball mill is presented. The obtained experimental results of application of different methods of introduction of SnO₂ nanoparticles in the silver matrix such as conventional powder metallurgy mixing and template method are given and discussed in terms of their influence on microstructure and physical properties (density, hardness and electrical conductivity) of the prepared Ag-SnO₂ electrical contact materials.

Keywords: silver-metal oxide contacts, processing, properties, oxide nanoparticles

Introduction
The silver based electrical contact materials are widely used by electrical and electronics industry representing a significant group of functional materials [1]. Basic properties required for these materials are high electrical and thermal conductivity, high resistance to arcing, high welding resistance, low contact resistance, high hardness and

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strength. For several decades Ag-CdO has been the material of choice for application in a wide range of switching devices [2]. This is due to its superior anti-welding properties and wear resistance, suitable hardness that enables good machineability and high electrical conductivity. Taking into consideration toxic nature of cadmium and strict environmental legislation (RoHS, WEEE) numerous materials have been investigated as a possible more environmentally friendly substitutes [3]. Among those, Ag-SnO₂ and Ag-ZnO have emerged as the most promising candidates [4]. As both materials do not always offer the same performance as Ag-CdO various attempts were carried out to enhance their performance mainly by introduction of small amounts of different metal oxides (In₂O₃, CuO, Bi₂O₃ or WO₃) [3-6]. The other important factor is dispersion of metal oxides in silver matrix as it is generally accepted that the performance of these materials can be improved by finer dispersion [7,8]. Considering that the oxide dispersion is directly related to the applied processing technique, a variety of production routes has been developed. The two dominant commercially used techniques are powder metallurgy and internal oxidation of silver alloys [9,10]. As both wet and dry mixing of powders reach the limit of applicability at particle sizes about 1-2 µm, in order to obtain homogenous microstructures containing fine metal oxide particles, internal oxidation, reactive milling or chemical precipitation are used. The internal oxidation route relies on ingot metallurgy processing to produce starting silver alloys by melting and casting. The prepared cast slabs are usually rolled with intermediate annealing and subsequently subjected to internal oxidation by heating in oxygen atmosphere.

Further improvement in homogeneity and finer dispersion can be achieved by methods based on chemical precipitation such as dual-jet or more recently bio casting or polymer assisted inorganic composite formation methods.

The presented study provides a brief overview of the experimental results of investigations of different production technologies and their influence on properties of silver based electrical contact materials, with emphasis on currently dominating Ag-SnO₂ materials. The most commonly used internal oxidation/ingot metallurgy and powder metallurgy methods are illustrated on example of Ag-CdO, Ag-ZnO and nanocrystalline Ag-SnO₂ materials. High energy ball milling route is utilized for preparation of homogenous Ag-SnO₂ powder mixtures. The influence of metal oxide nanoparticles and method of their introduction into the silver matrix on uniformity of microstructure and physical properties, such as: density, hardness and electrical conductivity of Ag-SnO₂ materials are also presented. In addition, some of the most common applications of the silver based electrical contact materials are discussed.

Materials and Processing

Internal oxidation/Ingot metallurgy

The internal oxidation route (IO) relies on ingot metallurgy processing to produce starting silver alloys by melting and casting. Ag-Cd alloys with 9.5 mass % of Cd were synthesized by melting of pure Ag and Cd metals (99.90 mass %). The prepared cast slabs were firstly homogenized at 600°C for 4 h in nitrogen atmosphere and subsequently plastically deformed with intermediate annealing at 600°C. Internal oxidation of the investigated alloys was carried out in electro-resistive oven in air atmosphere under natural convection of air at 670°C, 750°C and 795°C during 48 hours.

Technological procedure of the internal oxidation route for production of Ag-CdO electrical contact materials is given in Fig. 1.
Fig. 1 – Flowchart of the internal oxidation process of Ag-Cd alloys. Graphical representation of the influence of temperature and time on thickness of the oxidized layer is given in Fig. 2.

Fig. 2 - Dependence of thickness of oxidized layer of Ag-Cd alloys on temperature and duration of internal oxidation process.

The results presented in Fig. 2 demonstrate that at higher temperatures (795°C) oxidation rate is higher. Hence, for the applied synthesis conditions temperature has the dominant influence on the process of internal oxidation.
Microstructure of the prepared IO Ag-CdO electrical contact material is illustrated by the scanning electron microscopy (SEM) images given in Fig 3.

![Image](a)

![Image](b)

**Fig. 3 - Microstructure of the Ag-CdO prepared by internal oxidation process**

In the optimized process of oxidation high and homogenous dispersion of CdO in the silver matrix is obtained (Fig. 3). 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 is left unoxidized (Fig. 3b). More detailed information on influence of process parameters on oxidation kinetics is given in [10].
Powder metallurgy

Powder metallurgy method (PM) 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.

Studied PM Ag-ZnO (90:10) electrical contact materials were produced from pure silver powder obtained by chemical synthesis route and very fine commercial ZnO (99.0%) powder produced by Sigma-Aldrich.

The technological procedure included dry and wet homogenization of powder mixtures, pressing, sintering and additional mechanical treatment (forging) as illustrated in Fig. 4.

![Flowchart of the powder metallurgy process for production of Ag-ZnO and Ag-SnO₂ contact materials](image)

Since the starting powders were in the form of agglomerates consisting of very fine particles, homogenization of both wet and dry was done in several steps. 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 820°C in electro-resistive oven 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.

The microstructure of the PM Ag-ZnO (90:10) is given in Fig. 5. Microstructure appears to be less fine and more porous compared to IO contact material. Better connectivity of the silver grains can be observed as ZnO particles are predominantly situated on silver grain boundaries.

The influence of introduction of metal oxide nanoparticles in silver matrix is illustrated by preparation of Ag-SnO₂ (92:8) using powder metallurgy method. Commercial SnO₂ nano powder produced by Sigma-Aldrich (SnO₂ - 99.9%) was used for sample preparation. Particle size distribution and powder morphology of used silver
and tin-oxide powders are given in more detail in [8]. Considering the very fine particle sizes 40-100 nm of SnO₂ powder, prior to mixing particles were firstly suspended in weak ethanol aqueous solution and irradiated by ultrasound in order to de-agglomerate particles. Magnetic stirrer was used for wet mixing and homogenization of starting powders. The investigated samples of the Ag-SnO₂ electrical contacts were compacted into blocks with dimensions 25.4×11×3 mm, under pressure of 360 MPa. The obtained Ag-SnO₂ green compacts were then sintered for 3h at 820°C in electro-resistive oven in the air atmosphere. The samples were subsequently forged at 800°C with the low degree of reduction and then annealed at 750°C for 30 min followed by quenching in water.

![Fig. 5 – Metallographic SEM images of the Ag-ZnO prepared by powder metallurgy method](image-url)

Metallographic SEM images of the polished cross-sections of the prepared Ag-SnO₂ (92:8) contacts are presented in Fig. 6.
Fig. 6 - Microstructure of the Ag-SnO$_2$ with SnO$_2$ nanoparticles prepared by powder metallurgy method

It was found that the introduction of metal oxide nanoparticles will provide enhancement of oxide dispersion in silver matrix compared to the microparticle counterpart [8]. Nevertheless, as previously stated, this enhancement is limited by the nature of the applied preparation method. The presented microstructures exhibit somewhat greater homogeneity and lower porosity compared to the discussed Ag-ZnO material. Such microstructure will most certainly affect the structure dependent properties. With the reduction of the particle size higher hardness, i.e. lower ductility is expected as well as lower porosity due to better packing of the particles. On the other hand, although high hardness is desirable it is limited by the requirements for machineability of the material in subsequent fabrication to its final form. Another important issue is that electrical properties strongly depend on particle size and particle spacing.
High-energy ball milling

Considering the demand for high homogeneity of the Ag-SnO₂ material, one of the potential alternative processes for improvement of homogeneity is high energy ball milling or mechanochemical route. Depending on whether chemical reaction takes place in the mixture the process is referred to as reactive milling, mechanical alloying or mechanical mixing (MM). During high energy ball milling composite powder particles repeatedly undergo fracturing and rewelding which leads to very fine dispersion of SnO₂ particles in soft silver matrix [7]. The technological procedure of the high-energy ball milling is illustrated by the flowchart given in Fig. 7.

![Flowchart of the high-energy ball milling process (Ag-SnO₂)](image)

The prepared MM Ag-SnO₂ electrical contact materials were produced from pure silver powder obtained by chemical synthesis route and very fine commercial SnO₂ (99.9%) powder produced by Sigma-Aldrich in 92:8 weight ratio. The starting powders 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. The 5 mm tungsten carbide balls were used as grinding bodies.

The mixture was consolidated into Ø16 × 3 mm tablets under the 100 MPa pressure in a steel dye. The green compacts were sintered for 2h at 820°C in electro-resistive oven in the air atmosphere. After sintering, the density of the samples was improved by forging (at 800°C) with the low degree of reduction (~15%). The samples were subsequently annealed at 750°C for 30 min and then quenched in water.

Microstructure of the obtained MM Ag-SnO₂ contact materials is illustrated by the corresponding SEM images of the polished cross-sections given in Fig. 8.
Due to poor wettability of the tin oxide 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. 8b), after pressing and sintering, pure silver (denuded) zones can be observed which inevitably affect the structure dependent properties. The issue is commonly suppressed by introduction of special additives such as In$_2$O$_3$, WO$_3$ and MoO$_3$ in small quantities [11].

Although, the resulting powders are characterized by high dispersion they have tendency to exhibit significant inactivity during sintering [12].

Fig. 8 - Microstructure of the Ag-SnO$_2$ electrical contact materials prepared by high energy ball milling technique
Template method

For production of silver-metal oxide electrical contact materials with the highest degree of homogeneity different electroless chemical methods based on chemical precipitation or co-precipitation are used. Among which, recently developed polymer assisted inorganic nanocomposite formation [13] and bio-casting methods [14] that utilize different organic templates offer a lot of possibilities for preparation of very uniform nanocomposite structures.

For synthesis of the studied Ag-SnO<sub>2</sub> contact material by template method (TM), as precursors, commercial SnO<sub>2</sub> nanoparticles and commercial AgNO<sub>3</sub> powder were used as delivered. Used procedure is modified method developed by [15] which uses commercial ashless quantitative filter paper (Whatman Inc., burning ash < 0.005%) as the template. The method consists of several steps which include: preparation of AgNO<sub>3</sub> aqueous solution and SnO<sub>2</sub> nanoparticles suspension, mixing of precursors and impregnation of the template, drying and template removal process. Technological procedure of the template method of introduction of SnO<sub>2</sub> nanoparticles into silver matrix for preparation of Ag-SnO<sub>2</sub> composite powders used for production of Ag-SnO<sub>2</sub> contact materials is presented in Fig. 9.

In order to illustrate the influence of different production methods on microstructure and properties of the investigated Ag-SnO<sub>2</sub> materials were prepared with the same Ag:SnO<sub>2</sub> weight ratio (92:8).

![Flowchart of the template method of production Ag-SnO<sub>2</sub> composite powder](image)

After drying AgNO<sub>3</sub> crystallizes in pores of the filter paper and take their inner shape entrapping the dispersed SnO<sub>2</sub> nanoparticles within. During the template removal process, i.e. quick combustion it transforms to elemental Ag with embedded SnO<sub>2</sub>
nanoparticles. Additional calcination is performed in order to make sure that both processes are fully completed. The resulting morphology of the silver-tin oxide composite powder corresponds to pores structure of the filter paper. The presented SEM image (Fig. 10a) illustrates the mesh like structure of the composite powder. For the preparation of the final contact material the same powder metallurgy procedure was used as for the PM Ag-SnO$_2$ material with SnO$_2$ nanoparticles. Microstructure of the produced TM Ag-SnO$_2$ contact materials is illustrated by the corresponding SEM image of the polished cross-section given in Fig. 10b.

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**Fig. 10 - Ag-SnO$_2$ with SnO$_2$ nanoparticles prepared by template method:**

a) morphology of the composite powder and b) microstructure of the polished cross-section of the final contact material
Overview of physical properties of the studied silver-metal oxide contact materials

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 on polished cross-sections of the samples at room temperature. Density was determined by conventional method. Hardness measurements were carried out 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.

Important physical properties of the studied and presented silver-metal oxide electrical contact materials produced by different techniques are given in Table 1.

<table>
<thead>
<tr>
<th>Process</th>
<th>Composition</th>
<th>Density [g/cm³]</th>
<th>Hardness [HV5]</th>
<th>Conductivity [MS/m] [%IACS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal oxidation/ingot metallurgy</td>
<td>Ag-CdO (90:10)</td>
<td>9.65</td>
<td>90</td>
<td>45.34</td>
</tr>
<tr>
<td>Powder metallurgy</td>
<td>Ag-ZnO (90:10)</td>
<td>9.61</td>
<td>81</td>
<td>40.42</td>
</tr>
<tr>
<td>High-energy ball milling</td>
<td>Ag-SnO₂ nano (92:8)</td>
<td>9.69</td>
<td>108</td>
<td>37.28</td>
</tr>
<tr>
<td>Template method</td>
<td>Ag-SnO₂ nano (92:8)</td>
<td>9.80</td>
<td>124</td>
<td>43.52</td>
</tr>
</tbody>
</table>

Although the presented methods demonstrate preparation of different silver-metal oxide contact materials the overall trend of influence of applied preparation method on microstructure and structure dependent properties is evident.

Summary

The presented preparation methods are illustrated on the examples of some of the most commonly used silver-metal oxide electrical contact materials. Selection of the adequate contact material is governed by the application requirements and environmental legislation. As each of the presented methods is characterized by certain benefits, limitations and disadvantages selection of the production method is always a compromise between required functional properties, economic input and the volume of production.

The ingot metallurgy based internal oxidation method of production of silver-metal oxide contacts allows production of complex forms of electrical contacts more economically compared to many alternative methods and requires less production steps. It is particularly suitable for production of low ductile materials like Ag-SnO₂ that are difficult to fabricate because of poor metallurgical properties. Even though the produced
microstructures are very uniform the method is governed by the diffusion of the oxygen into the alloy and presence of the denuded zones can be expected. On the other hand, methods that follow the powder metallurgy route offer possibility for production of contacts with variety of compositions, including use of different metal oxides simultaneously. This is very important advantage since it enables tailoring and enhancement of contact’s properties and thus increases the latitude of potential applications. Disadvantage of these methods is that produced materials inherently possess certain degree of porosity that has significant impact on functional properties. Use of finer powders reduces this problem to some extent however it meets a variety of different limitations ranging from introduction of particles and mixing to required homogeneity of microstructure. Methods for composite powder preparation such as discussed high-energy ball milling and template method overcome most of these issues and provide a very high degree of dispersion. Nonetheless, high-energy milled composite powders may exhibit significant inactivity during sintering. Template method can be quite time demanding and the choice of adequate template material is essential, since template removal process can complicate process significantly.

Application area of silver-metal oxide based electrical contact materials is very wide and covers almost every industry, ranging from information and data technology, automotive electrics, automation, control and regulating technology to low, medium and high voltage energy technology. General applications include numerous electrical switching devices and switchgear such as high-voltage switchgear, industrial and installation switchgear, switches for home appliances, switchgear and switches for railways, electrically powered and motor vehicles.

Owing to development of silver alloys produced by ingot metallurgy processes, sintered materials produced by powder metallurgy and introduction of modern production methods, the properties of the silver electrical contact materials are considerably improved and extended to meet a wide range of demands. Hence, today the end users have a selection of Ag based contacts at their disposal that can be optimally selected to the specific application.

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References