

AgSnO₂ sintered electrical contacts with ultrafine and uniformly dispersed microstructure

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The paper presents the research results concerning the preparation of some advanced materials starting from AgSnO₂ very fine powders mixtures, having microcrystalline sizes obtained by chemical methods. These powders were processed by powder metallurgy techniques in order to manufacture some electrical contacts for low voltage devices working in air. The materials were characterized during the whole technological flow. Comparatively, there are presented the physical, mechanical, electrical, microstructural and functional characteristics of the sintered electrical contacts from powder mixtures obtained by chemical and mechanical methods. The fine and uniformly dispersed microstructure leads to the improvement of the functional characteristics of the electrical contacts: behavior at the electrical erosion, sticking, overtemperature and arc quenching.

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1. Introduction

Up to now AgCdO has been the preferred material for electrical contacts used in almost all low voltage devices of contactors type due to its excellent functional and technological properties. AgCdO material has anti-welding and antierosion properties combined with constant resistance, examples of advantageous well-combined properties. Another favorable quality is that it has a good processing capability [1].

Nowadays, the AgSnO₂ non toxic material is recommended for the replacement of the toxic and carcinogenic AgCdO material [2-4]. Like AgCdO contacts, AgSnO₂ can be produced by powder metallurgy techniques [5-7]. AgSnO₂ materials develop a slightly higher contact resistance than the AgCdO ones due to thermal stability of SnO₂. A WO₃ addition improves sinterability, wettability electrical erosion, and overheating behavior. However, some unfavorable effects, like brittleness and material transfer during switching operations can occur [8-10].

The novelty of our work consists in the obtaining of some AgSnO₂ electrical contacts doped with WO₃ having an ultra fine and a uniformly dispersed microstructure, from chemical precipitated powder mixtures of microcrystalline size. Their preparation and characterization is presented comparatively with the AgSnO₂ classical preparation by mechanical mixtures.

2. Experimental

The experiments were performed in both cases on materials with a chemical composition of 90 wt. % Ag, 9.5 wt. % SnO₂ and 0.5 wt. % WO₃, noticed as Ag:SnO₂:WO₃ (90:9.5:0.5). We chose this composition based on our previous researches in this field [11 - 12].

The Ag:SnO₂:WO₃ powders mixtures were obtained by chemical precipitation and mechanical mixing.

The first method for the obtaining of powders mixtures consists in the Ag precipitation from an AgNO₃ aqueous solution containing a suspension of SnO₂ and WO₃ particles. Some aqueous solutions of NaOH, Na₂CO₃·10H₂O, H₂C₂O₄·2H₂O or (NH₄)₂C₂O₄·H₂O were used as precipitants. The precipitates were filtered, dried at 100 °C for 3 hours, calcined in air at 450...550 °C for 2...4 hours, washed and dried at 100 °C for 3 hours.

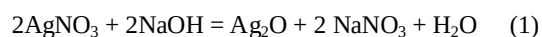
The second method for the obtaining of powders mixtures consists in mechanical homogenization of the Ag, SnO₂ and WO₃ powders in a ratio of (90:9.5:0.5), using a steel balls mixer of Turbula type, for 4 hours.

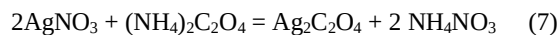
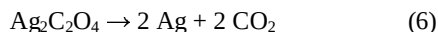
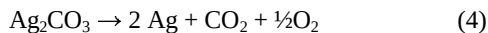
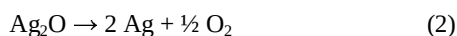
We used the following notations for the chemical mixtures: CM-I (precipitated by NaOH), CM-II (precipitated by Na₂CO₃·10H₂O), CM-III (precipitated by H₂C₂O₄·2H₂O), and CM-IV, precipitated by (NH₄)₂C₂O₄·H₂O, and for the mechanical mixture: MM.

The powder mixtures were processed by granulation, compacting at 300 MPa, sintering in air at 850 °C for 2 hours, repressing at 900 MPa and soft annealing at 720 °C for 30 minutes. The electrical contacts destined for the functional tests were obtained in the same shapes and dimensions like the AgCdO contacts, used usually in contactors of RG 200 A type.

The optimum processing parameters were established as a result of some intensive tests and analyses of chemical, thermal-differential, X-ray, grain size, morphological, microstructural, electrical, and mechanical type.

The chemical compositions were determined by the standard gravimetric methods and the reaction yield was evaluated according to the stoichiometry of the reactions:





The X-ray diffraction patterns were recorded graphically using a Philips diffractometer with a Cu anode and interpreted with Philips XPert Graphics & Identifier software.

The mean diameter of particles, named d_{FSSS} (Fisher Sub Sieve Size diameter), was measured on a Fisher Sieve tester, by its graphically recording.

The particle morphology of CM powder mixtures and the microstructure of the CM electrical contacts were studied by Scanning Electronic Microscopy (SEM) with a Philips XL 30 electronic microscope. The electrical contact microstructure images were obtained on un-etched and polished samples put in resin.

The microstructure of the MM electrical contacts, and the jonction of MM contact layer with silver soldering layer was analyzed using a Carl Zeiss optical microscope of NU 2 type.

The electrical resistivity was calculated as the inverse ratio of the electrical conductivity, which was directly measured at room temperature with a SIGMASCOP - EX 8 device.

The Brinell/Vickers hardness was performed on a hardness tester of WPM-Leipzig type, in standard conditions.

The functional tests (overttemperature, making and breaking capacity, and lifetime) were performed on an especial stand for the testing of the electrical devices, using 5 contactors of RG 200 type, each of them fitted with six pairs of contacts (fixed and mobile), in AC3 regime, at $I_n = 200 \text{ A}$, $U_e = 3 \times 400 \text{ V}$, $f = 50 \text{ Hz}$ and an operating rate of 600 cycles/hour, according to the international standard CEI 947 – 4 – 1 : 1990.

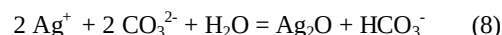
3. Results and discussion

The composition of the chemical mixtures and the reaction yield are presented in Table 1. As we can see from Table 1, the chemical precipitation reactions of all mixtures types occur with a high efficiency. The conversion level of the precipitates decomposition is close to theoretical values, too.

Table 1. The compositions of the chemical mixtures and the reaction yield.

Name of powder mixture	Chemical composition, wt. %			Reaction yield, %
	Ag	SnO ₂	WO ₃	
CM – I	89.76	9.73	0.51	98.3
CM – II	89.80	9.69	0.51	99.1
CM – III	89.72	9.77	0.51	98.1
CM – IV	89.73	9.76	0.51	98.1

By calcination, Ag_2CO_3 is decomposed in two stages with degassing of CO_2 and O_2 according to equations no. (2) and no. (4). Ag_2CO_3 is decomposed theoretically at 218 °C, and Ag_2O at 300 °C. An excess of alkaline carbonate leads to Ag_2O formation. Also, when Ag_2CO_3 is precipitated with a too much diluted solution of Na_2CO_3 a contamination with Ag_2O occurs.



In Fig. 1a) that was recorded for CM - II powder before Ag_2CO_3 decomposition, the specific lines of SnO_2 and Ag_2CO_3 are revealed. The presence of some Ag_2O small quantities is the result of working conditions according to equation no. (8). Due to small addition of WO_3 , it was not identified. In Fig 1 b) that was recorded for CM - II powder after calcination, there are revealed only the specific lines of SnO_2 and Ag. Also, WO_3 was not identified because it was under the diffractometer detection limit. The decomposition of silver precipitates occurs at low temperatures without sintering or chemical compounds forming in the final powders mixtures. The chemical and X-ray analyses carried out for chemical mixtures show a complete decomposition of all precipitates to metallic silver.

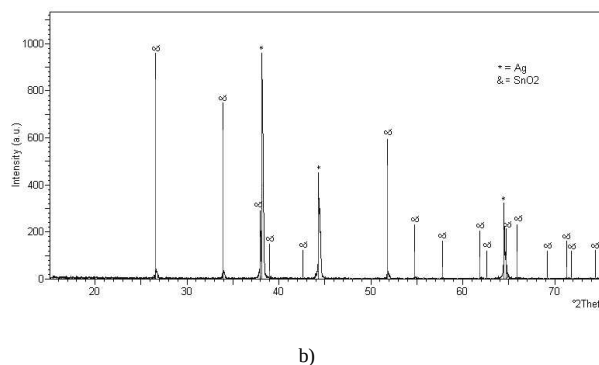
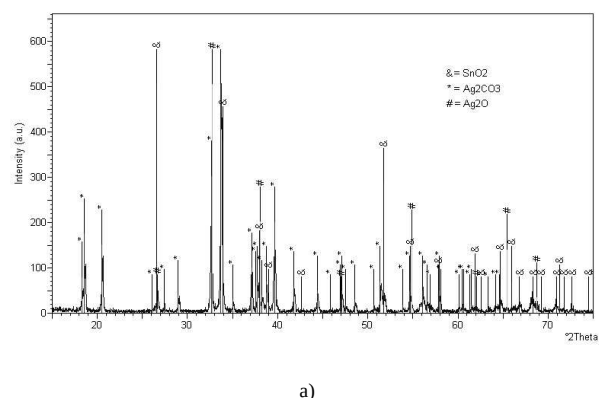


Fig. 1. XRD patterns of the CM – II powder: (a) before and (b) after Ag_2CO_3 decomposition.

The physical properties and particles characteristics of the starting powders used for MM powder obtaining are shown in Table 2. In Table 3 are presented some grain

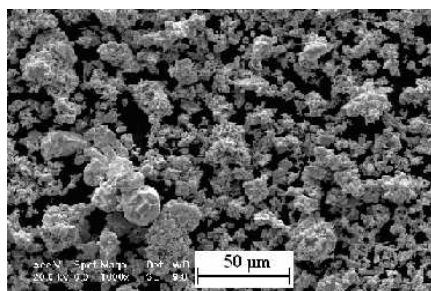
characteristics. The specific surface of the powders was calculated with equation no. (8). Fig. 2 presents the morphological aspects of the initial powders and CM powders.

Table 2. The physical properties and particle characteristics of the Ag, SnO₂ and WO₃ powders.

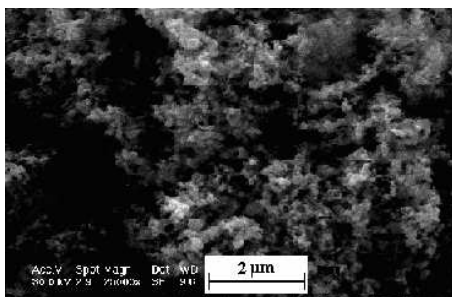
Name of powder	Purity, %	Melting point, °C	Theoretical density, g/cm ³	Bulk density, g/cm ³	d _{FSSS} , μm	d _{max} , μm	Specific surface, m ² /g
Ag	min 99.9	961	10.50	1.70	10	32	5.71
SnO ₂	min 99.0	1127	6.95	0.38	1	5	86.58
WO ₃	min 99.6	1473	7.16	0.87	0.5	2	167.59

Table 3. The characteristics of the powder mixtures.

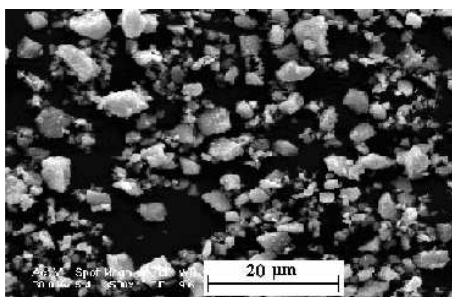
Powder mixture type	Bulk density, g/cm ³	d _{FSSS} , μm	d _{max} , μm	Specific surface, m ² /g
CM – I	2.20	3.40	15	17.68
CM – II	1.92	1.38	5	43.56
CM – III	1.02	1.05	2	57.26
CM – IV	0.98	0.98	2	61.35
MM	2.65	10	32	6.01



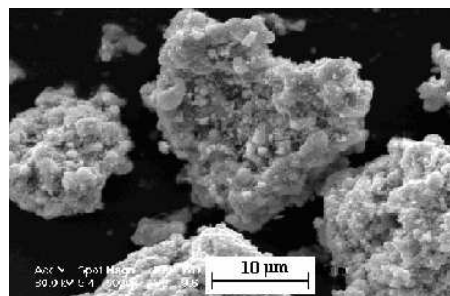
a)



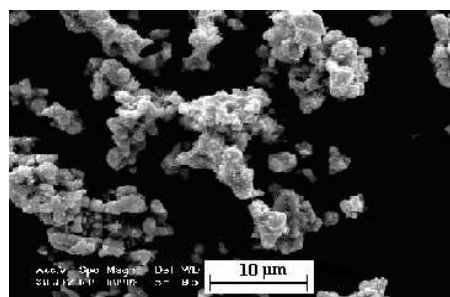
b)



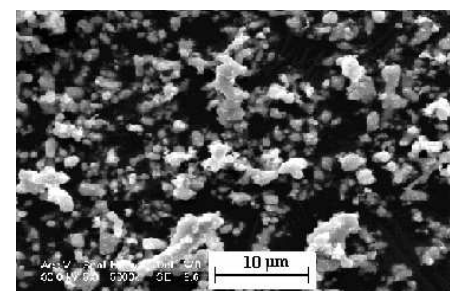
c)



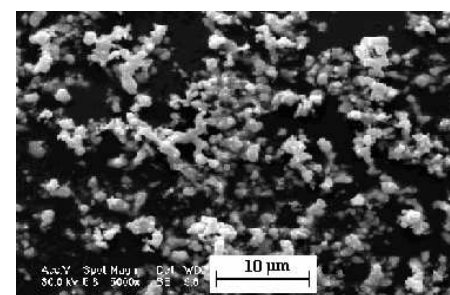
d)



e)



f)



g)

Fig. 2. The SEM morphological aspects of the powders: a) Ag, b) SnO₂, c) WO₃, d) CM-I, e) CM-II, f) CM-III, and g) CM-IV.

The Ag powder particles have a dendritic shape specific to those obtained by electrochemical methods. The SnO₂ powder was obtained by chemical methods and its particles have an irregular shape. Also, the WO₃ powder was obtained by chemical methods (by ammonium

paratungstate decomposition) and its particles have rhomboidal shape. CM - I powder is very fine but it is presented as large agglomerated particles. CM - II, CM - III and CM - IV powders are very fine, in the range of microcrystalline grains and they present a low tendency to agglomeration.

In Fig. 3 are shown the compressibility curves of the powders mixtures. The flowability of the un-granulated powders for the all powders mixtures is poor. But the granulated powders present a good flowability, a very good behavior at handling and they can be pressed automatically.

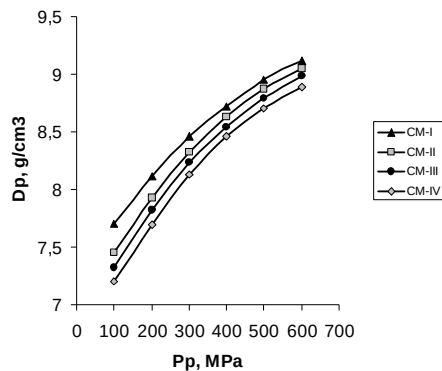
The compressibility of the CM powders is greater than of the MM powder. Also, the sinterability of the CM chemical samples is better than the mechanical ones, because the specific surface is higher for the CM materials that are made of ultra fine powders.

Table 4 presents some physical and mechanical characteristics of the Ag:SnO₂:WO₃ (90:9.5:0.5) electrical contacts. Based on the data presented in Table 4, we calculated the remnant porosity, which decreases in the series: MM, CM - I, CM - IV, CM - III, and CM - II, having the following values: 6.11 %, 5.61 %, 4.91 %, 4.81 % and 4.31 %. Another observation is that the density, the hardness and the electrical conductivity of the electrical contacts increase in the same series.

Table 4. Physical and mechanical characteristics of the Ag:SnO₂:WO₃ (90:9.5:0.5) electrical contacts.

Material type	Realized density, g/cm ³	Relative density, %	Hardness, HB		Hardness, HV		Resistivity, μΩ cm
			hard	soft	hard	soft	
CM - I	9.42	94.39	97	90	102	96	2.6
CM - II	9.55	95.69	110	94	115	104	2.5
CM - III	9.50	95.19	105	92	114	103	2.7
CM - IV	9.49	95.09	104	91	111	100	2.7
MM	9.37	93.89	81	78	85	82	2.7

In Fig. 4 are presented the SEM images of the CM electrical contacts, and in Fig. 5 is presented the optical image of the MM electrical contacts. Due to the coarser grain sizes of MM particles, the microstructure analysis was performed on optical microscope. In Fig. 6 is shown the cross section optical image of an electrical contact brazed on a copper holder.



a)

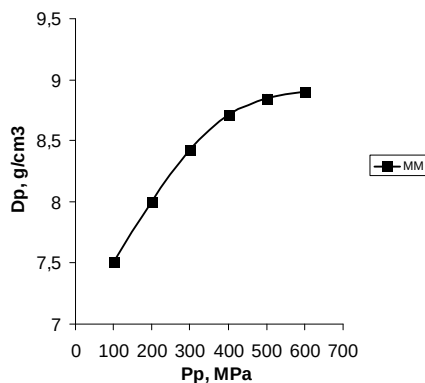
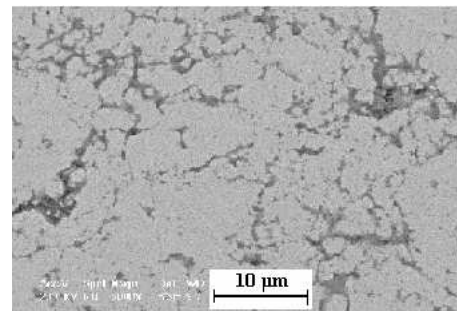
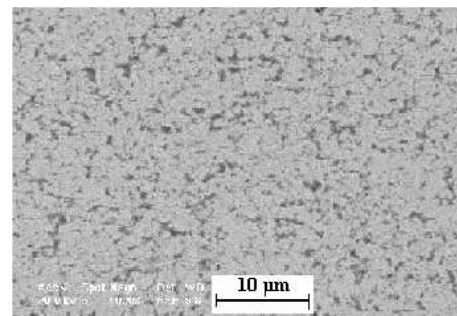


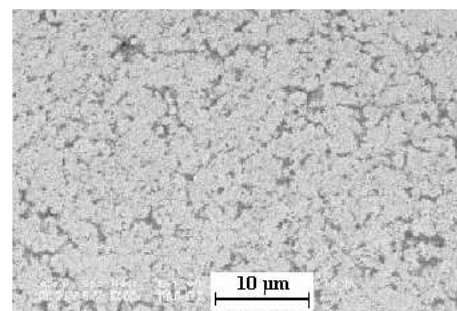
Fig. 3. The compressibility curves of the powder mixtures.



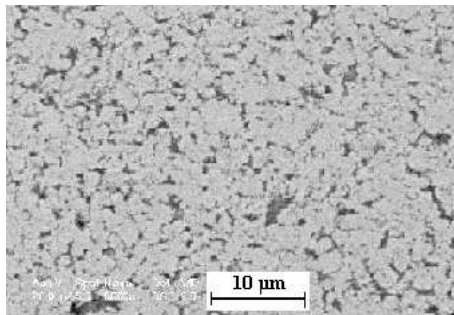
a



b



c



d

Fig. 4. The SEM images of the Ag-SnO₂-WO₃-90-9.5-0.5 electrical contacts: a) CM - I, b) CM - II, c) CM - III, d) CM - IV.

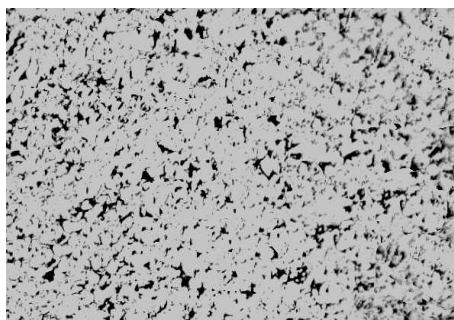


Fig. 5. The optical image of the MM Ag-SnO₂-WO₃-90-9.5-0.5 electrical contacts.

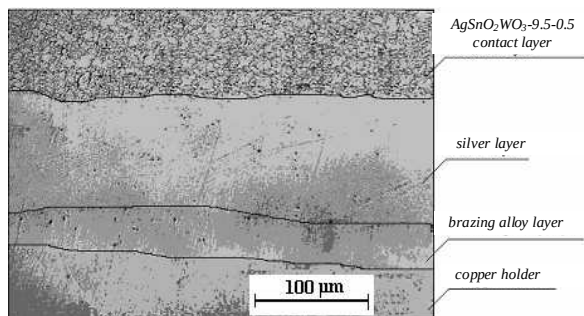


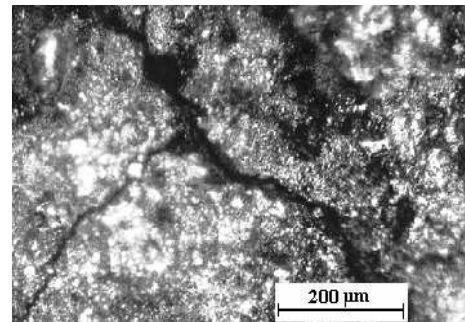
Fig. 6. Cross section optical image of an electrical contact brazed on a copper holder.

In the series of CM materials, the oxide components are uniformly and finely dispersed in the silver matrix, excepting the CM - I where some agglomerated particles are observed.

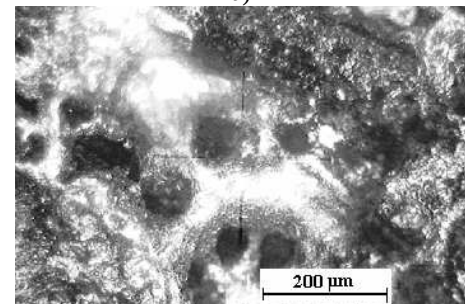
The best results from the physical, mechanical and electrical point of view were obtained for the CM - II material, namely the chemical mixed powders precipitated with Na₂CO₃·10H₂O. This precipitation agent is ecological and than cheaper the other precipitation agents. Also, in the case of its using, the precipitation reaction occurs in better conditions than the other cases. As a result, the filtration of powder mixture is performed much easier,

and Ag₂CO₃ obtained after the precipitation is decomposed in better conditions. Therefore, we performed the functional tests with the CM - II material on contactors of I_n = 200 A, in AC3 regime.

The lifetime of the Ag:SnO₂:WO₃ (90:9.5:0.5) electrical contacts tested in contactors working at I_n = 200 A in AC3 regime was of 300.000 manoeuvring cycles, being the same as the AgCdO one, without any especial improving of the devices. The optical images of the contact piece surface at the lifetime ending are presented in Fig. 7.



a)



b)

Fig. 7. Optical images of the contact piece surface at the lifetime ending: (a) fixed and (b) mobile contacts.

Some cracks, melted metallic drops, holes and breaks can be observed. Also, there is a uniform wearing of the contact surface, which leads to the same distribution of the mechanical strengths in the material.

The CM - II electrical contacts had a good behavior at arc quenching, overtemperature, sticking and electrical erosion, according to the standard in force.

4. Conclusions

In order to obtain some electrical contacts with improved functional properties we developed intensive researches. We prepared some new advanced AgSnO₂ electrical contact materials starting from powder mixtures obtained by chemical precipitation way.

The results of the characterization of the Ag-SnO₂-WO₃ new material showed that its physical, mechanical and functional properties are comparatively to

the AgCdO one, especially the materials obtained by chemical powder mixtures. The last ones, being manufactured from some very fine powders, which have a high specific surface and a good sinterability, present an improved microstructure: the components are uniformly and finely dispersed and the porosity is very low. As a result, a good density, hardness and electrical conductivity were obtained.

From the functional point of view, the Ag-SnO₂-WO₃ (90:9.5:0.5) electrical contacts proved a good behavior at $I_n = 200$ A and in AC3 working regime, successfully replacing the classical AgCdO electrical contacts, without any especial improving of the devices. This is due mainly to their superior overtemperature behavior.

The new electrical contacts present many advantages from the technical, economical and environmental point of view.

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