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New Ag-SnO_2-MeO ecological advanced materials for electrical contacts used in electromagnetic contactors

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The paper presents the research results about the achievement and characterization of some new Ag-SnO_2-MeO (MeO = Bi_2O_3 and CuO) ecological electrical contact materials as substitutes of the toxic and carcinogenic Ag-CdO ones. The new materials were obtained from very fine and uniform Ag-SnO_2 chemical powders mixtures doped with MeO. These were realized by a wet way, in an $AgNO_3$ aqueous solution containing SnO_2 and MeO particles in suspension, by Ag precipitation „in situ" with a $Na_2CO_3 \cdot 10H_2O$ aqueous solution. The obtained mixtures were filtered, washed, dried, calcined to the desired final composition, washed again to remove the impurities and dried. Then these were processed by powder metallurgy techniques in form of electrical contact pieces fitted in AC electromagnetic contactors working in air at I_{th} = 125 A and I_n = 107 A. The materials were characterized from the physical, mechanical, electrical, microstructural and functional points of view.

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Keywords: Ag-SnO_2-MeO, Contact materials, Electromagnetic contactors

1. Introduction

At present, the Ag-SnO_2 electrical contact materials are in the top of the researches due to the need to improve their contact characteristics so that to be as close as possible to the ones of the classical Ag-CdO. In air low voltage switching apparatuses, Ag-CdO materials proved the best electrical, technological and functional characteristics such as: very high electrical and thermal conductibilities, a good workability, a high resistance against arc erosion and welding, a low contact resistance, and a very good arc quenching ability. However, their major inconveniences are the toxicity both in service and in the technological processes due to the carcinogenic effect of Cd and CdO upon human bodies and environment, too. Therefore, in accordance to the normatives in force, already in many countries Ag-CdO production was gradually reduced or totally removed [1, 2].

The novelty of our works consists in the obtaining of some new environmental friendly Ag-SnO_2-MeO contact materials with an improved microstructure as well as improved technological, electrical and functional characteristics, especially due to the effect of the dopping agents. Also these materials can be used successfully in DC or AC contactors of nominal currents up to 3000 A, circuit breakers and relays [3…6].

2. Experiments

2.1. Materials and equipment

The *starting materials* used in the experiments: bidistilled water, crystallized $AgNO_3$ (Fluka, p.a. purity ≥ 99.5 %), $Na_2CO_3 \cdot 10H_2O$ (Fluka, purity ≥ 99.5 %), SnO_2 (Merck, purity min 99.0 %, d_{FSSS} = 1 μm, d_{max} = 5 μm), Bi_2O_3 (Riedl, purity min. 99.6 %, d_{FSSS} = 3.3 μm, d_{max} = 10 μm, CuO (Merck, purity min 99.0 %, d_{FSSS} = 0.45 μm, d_{max} = 10 μm)

The *equipment used for the obtaining and the characterization of the powders mixtures*: analitical balance (Precisa XT 220 A), ultrasonic bath (Falc Marvel), mechanical stirrer (Heidolph RZR 2021), pH-multimeter (Consort C830), vacuum oven (Vaciotem-T), oven working in controlled athmosphere (Nabertherm N7/H), derivatograph (Netzsch), Fisher Sieve tester, X-ray diffractometer (Philips), SEM (Philips XL 30).

The *equipment used for the obtaining and the characterization of the electrical contact pieces*: analitical balance (Precisa XT 220 A), granulator, crusher, automatic hydraulic press of F_{max} = 245 kN (Meyer), oven working in controlled athmosphere (Nabertherm N7/H), hydrostatic balance (Mettler Toledo XS 204), HB and HV hardness tester (WPM-Leipzig), conductivemeter (Sigmascope EX 8), micrometer (Schut), optical microscope (Carl Zeiss NU 2).

The *apparatuses used for the performing of the functional tests:* acquiring data system (Keithley), digital oscilloscope (Tektronix), transformers for current measuring (Metra), ampermeters, electric timekeeper, thermometer, hygrometer, voltmeter, cosfimeter, shunts.

2.2. Method

In our researches, some new Ag-SnO_2-MeO 90-9.3-0.7 contact materials were manufactured by classical powder metallurgy (PM) techniques from very fine and

uniform Ag-SnO_2 chemical powders mixtures doped with MeO (MeO = Bi_2O_3 and CuO). The powder mixtures were obtained as follows: Ag was precipitated from an $AgNO_3$ aqueous solution containing SnO_2 and MeO particles kept in suspension by a strong stirring using as precipitant a $Na_2CO_3 \cdot 10H_2O$ aqueous solution in a quantity necessary for its wholly set down. After that, the powders mixtures were filtered, dried in vacuum at 80 °C for 3 hours, and calcined in air at 450…550 °C for 2 hours to decompose the Ag precipitated compounds. Then the powders mixtures were washed to remove the impurities and dried in vacuum at 80 °C for 3 hours.

In order to be assured a good flowability of the powders mixtures, these were granulated. For the new contact materials obtaining, the optimal processing parameters were established, as follows: pressing pressure P_p = 300 MPa, sintering temperature T_s = 850 °C, sintering time t_s = 2 h, heating rate = 4 °C/min, repressing pressure P_r = 900 MPa, annealing temperature T_a = 720 °C and annealing time t_a = 0.5 h.

The samples were pressed in a double layer consisting of an Ag layer (for brazing of the pieces on the support) and an Ag-SnO_2-MeO 90-9.3-0.7 layer, in cylindrical forms with plane (fixed contacts) and spherical (mobile contacts) surfaces.

After repressing, the final pieces have sizes of ø 9.9 mm and h = 2.1 mm for the fixed contacts, respectively of ø 9.9 mm, h = 2.1 mm and R = 18 mm for the mobile contacts being suitable to be used in AC electromagnetic contactors working in air at I_{th} = 125 A and I_n = 107 A.

During the experiments, the Ag-SnO_2-Bi_2O_3-CuO obtained materials were characterized from physical, mechanical, electrical and microstructural point of view. Depending on their chemical composition, we codified these materials in this way: CM1 for 90-9.3-0.2-0.5 composition, CM2 for 90-9.3-0.35-0.35 composition, and CM3 for 90-9.3-0.5-0.2 composition.

The functional tests (making and breaking capacity, and conventional working in service) of the electrical contact pieces were performed according to IEC 947–4–1:1992 and SR EN 60947–4–1:2001 standards on five contactors, each of them fitted with six pairs of contacts (fixed and mobile) brazed on copper supports, working in air in AC3 regime, at conventional thermal current I_{th} = 125 A, nominal current I_n = 107 A, utilization nominal voltage U_n = 400 V, isolation nominal voltage U_i = 1000 V, nominal power P_n = 55 kW and nominal frequency = 50/60 Hz. Making and breaking capacity tests were performed for 50 manoeuvring cycles, and conventional working in service tests were performed for 6000 manoeuvring cycles.

3. Results and discussion

The decomposition in argon of the Ag_2CO_3 + SnO_2 + MeO precursors mixture carried out by thermal-differential analyses on a powder sample of 12.3 mg weight is presented in Fig. 1.

In Fig. 1 it is observed that the range of 160.8 – 306.2 °C shows the beginning of Ag_2CO_3 decomposition with a maxim at 195 °C, and the range of 306.2 – 375 °C shows the final phase of Ag_2O decomposition with a maxim at 353 °C. The final decomposition led to a total weight loss of 18.39 %, that is in accordance to the theoretical weight loss. Therefore, in our experiments the Ag precipitates decomposition occurred at a low temperature without their presintering or forming of some chemical compounds in final powders mixtures.

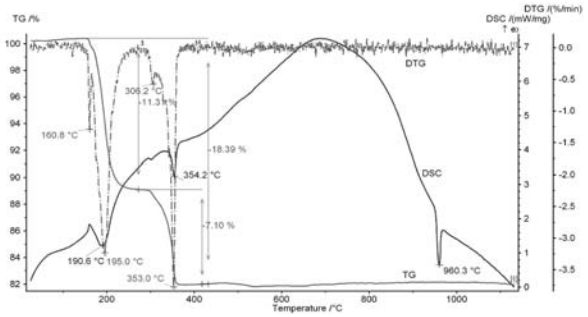


Fig. 1. TG, DTG and DTG decomposition curves of the Ag_2CO_3 + SnO_2 + MeO precursors mixture.

In Fig. 2 are shown the XRD patterns of the Ag-SnO_2-MeO 90-9.3-0.7 powders mixtures before (Fig. 2, a), and after Ag_2CO_3 decomposition (Fig. 2, b).

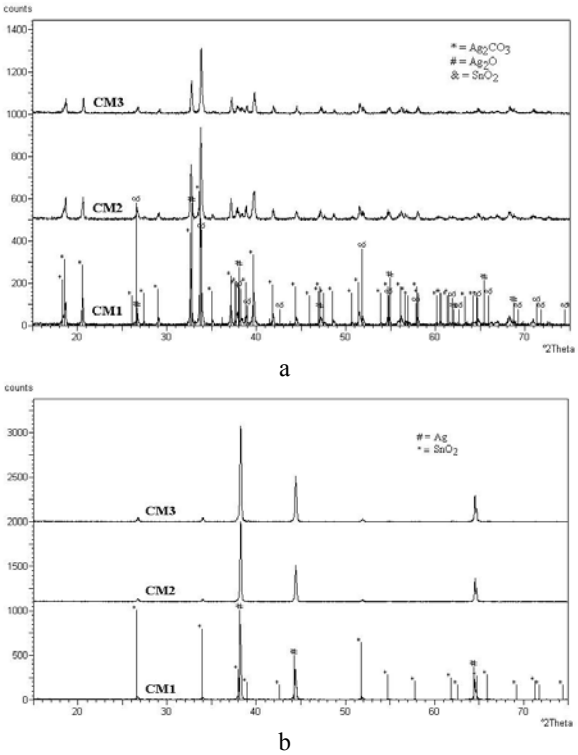


Fig. 2. XRD patterns of the Ag-SnO_2-MeO 90-9.3-0.7 powders mixtures: (a) before and (b) after Ag_2CO_3 decomposition.

In the first X-ray spectrum, the specific lines of SnO_2, Ag_2CO_3 and Ag_2O_3 are observed. In the second X-ray spectrum, only the specific lines of SnO_2 and Ag are noticed, proving that the complete decomposition of the all precipitates occurred to metallic silver. In both spectra, the presence of Bi_2O_3 and CuO was not identified due to their very small concentration of 0.7 wt. % that is under the diffractometer detection limit.

In Table 1 are presented some grain characteristics of the Ag-SnO_2-MeO 90-9.3-0.7 powders mixtures, which show that these powders are ultrafine ones.

Table 1. Some grain characteristics of the Ag-SnO_2-MeO 90-9.3-0.7 powders mixtures.

Powders mixtures type	Bulk density, g/cm^3		d_{FSSS}, μm	d_{max}, μm
	un-granulated powder	granulated powder		
CM1	1.09	2.53	1.28	5
CM2	0.90	2.51	1.26	5
CM3	1.10	2.54	1.29	5

Because the un-granulated powders mixtures do not flow due to the finesse of the the powders, we granulated them. The flowability of all granulated powders mixtures was of 12 s/50 g, which led to a good pressability.

The pressing density was of 7.8 g/cm^3 for manufacturing both fixed and mobile electrical contact pieces.

The obtained ultrafine powders mixtures had a high specific surface that assured a high sinterability. Moreover, the using of both Bi_2O_3 and CuO in doping of the Ag-SnO_2 material, led to high volumic contractions of the sintered pieces of 12.97…13.35 % for CM1, 11...11.32 % for CM2, and 15.68...15.89 % for CM3. As a result, the technological behavior of the electrical contact pieces was improved. Also, these sintered materials have better volumic contractions than Ag-SnO_2-MeO sintered pieces doped with a single MeO and obtained from chemical powders mixtures. For example, Ag-SnO_2-MeO 90-9.5-0.5 sintered materials manufactured in the same conditions as the contact materials presented in this paper, had volumic contractions of 5.52...5.77 % for MeO = Bi_2O_3 and of 7.96...8.15 % for MeO = CuO.

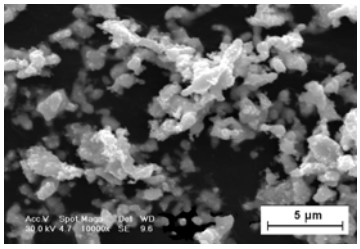
In Table 2 are shown some physical, mechanical and electrical characteristics of the final electrical contact pieces.

Table 2. Some physical, mechanical and electrical characteristics of the final electrical contact pieces.

Material type	Realized density, g/cm^3	Relative density, %	Hardness, daN/mm^2				Resistivity, μΩ·cm
			HB		HV		
			hard	soft	hard	soft	
CM1	9.70	97.14	98	85	103	92	2.29
CM2	9.61	96.18	101	87	107	94	2.38
CM3	9.72	97.21	103	89	109	95	2.24

For the all obtained contact materials, the realized density was close to the theoretical one. Thus, the remnant porosity decreases in the series: CM2, CM1 and CM3, having the following values: 3.82 %, 2.86 % and 2.79 %. Even the all materials present very good physical, mechanical and electrical properties, the best one proved to be the CM3 one.

In Fig. 3 are shown the SEM images of the Ag-SnO_2-MeO 90-9.3-0.7 powders mixtures.



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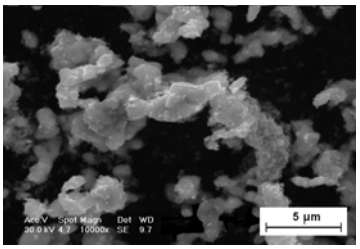

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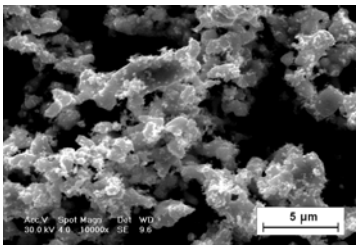
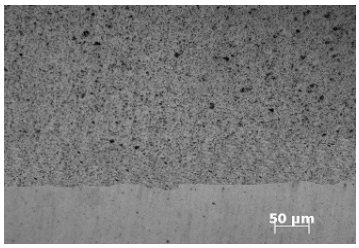


c

Fig. 3. The morphological aspect of the Ag-SnO_2-MeO 90-9.3-0.7 powders mixtures: a) CM1, b) CM2, c) CM3.

In Fig. 3 can be observed the particles are very fine and can be included in the microcrystalline range. Also, the powders mixtures had a low agglomeration tendency.

In Fig. 4 are shown the microstructural images of the electrical contact pieces manufactured from the Ag-SnO_2-MeO 90-9.3-0.7 powders mixtures.



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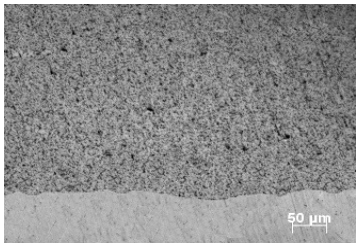

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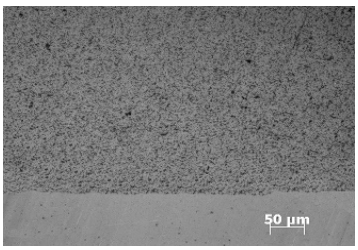

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Fig. 4. The microstructural images of the Ag-SnO_2-MeO 90-9.3-0.7 electrical contact pieces: a) CM1, b) CM2, c) CM3.

The microstructural analyses, carried out on the Ag-SnO_2-MeO 90-9.3-0.7 sintered materials showed very fine and uniform dispersions of the metal oxides in the silver matrix. Thus, improved physical-mechanical, electrical, microstructural and technological characteristics of the electrical contact pieces were achieved.

In Table 3 are presented the obtained results comparatively with the imposed values by the IEC 947–4–1:1992 and SR EN 60947–4–1:2001 standards for making and breaking capacity tests, and for conventional working in service tests [7, 8].

Table 3. The results obtained at the functional tests for the studied contact materials.

Functional tests / **Specific parameters**	**Making capacity**		**Making and breaking capacity**		**Conventional working in service**	
	Imposed values	**Measured values**	**Imposed values**	**Measured values**	**Imposed values**	**Measured values**
Applied voltage [V]	420…483	425	-	-	-	-
Making current [A]	1070…1230	1080	-	-	-	-
Remaking voltage at 50 Hz [V]	-	-	420…483	420	420…483	425
Making and breaking current [A]	-	-	856…985	860…862	118…136	120…126
Cos φ	0.3…0.4	0.36…0.365	0.3…0.4	0.365	0.4…0.5	0.46…0.47
Passing current duration [s]	~ 0.05	0.07…0.08	~ 0.05	0.06…0.07	~ 0.05	0.1
Break duration [s]	10	10	100	100	30	30
Oscillation frequency [kHz]	-	-	93…113	98…108	-	-
Over oscillation factor	-	-	1.05…1.15	1.07…1.125	-	-

The results obtained at the functional tests carried out on the Ag-SnO_2-MeO 90-9.3-0.7 electrical contact pieces proved that these advanced contact materials corresponded to the acceptance testing criteria imposed by the specific standards in force. During the functional tests, neither a permanent electrical arc nor contacts welding occurred. Also, the tested electrical contact pieces had a low contact resistance and a high lifetime, comparatively to the one of Ag-CdO 88-12 materials.

Also, the using of two metallic oxides (Bi_2O_3 and CuO) as dopping agents in 0.7 wt. % led to the improving of the technological, electrical and functional properties of the Ag-SnO_2 materials. These are superior than in the case of using of a single dopant in 0.2...0.5 wt. %, as can be observed in the research data presented in our previously papers for Ag-SnO_2 90-10 materials doped only with Bi_2O_3 or CuO [5].

4. Conclusions

The obtained Ag-SnO_2-MeO ecological contact materials showed both an improved microstructure and improved technological, electrical and functional characteristics, especially in hard exploitation conditions.

The characteristics and prices of these new materials are comparable to the Ag-CdO materials ones. Also, their use in switching apparatuses does not need any significant changes in the apparatuses design.

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