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A comparative study concerning the obtaining and using of some Ag-CdO, Ag-ZnO and Ag-SnO_2 sintered electrical contact materials

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In this paper is presented a comparative evaluation study concerning the methods of getting some electrical contact materials on silver basis, containing 90 wt. % Ag and 10 wt. % metallic oxides, namely CdO, ZnO or SnO_2. Two technological routes of powder mixtures preparation have been adopted: mechanical homogenization and chemical precipitation, respect ively. The influence of the oxide phase type upon the physical and mechanical characteristics and upon the functional behaviour of these materials included as electrical contacts in electromagnetic contactors of I_n = 40 A, working in air has been established. All the types of studied materials fulfilled to the normative in force concerning the functional characteristics. Some small differences were noticed regarding to the electrical erosion behaviour.

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1. Introduction

In the electric make/break low voltage switching devices working in air, such as AC or DC contactors, automatic circuit breakers or relays, the sintered electrical contact materials of Ag-MeO (MeO = CdO, ZnO or SnO_2) type can be used with good results [1...12]. The usefulness of these materials depends on a variety of electrical and mechanical properties, service life, load conditions and economics.

The Ag-CdO electrical contact materials have excellent functional properties in service and a long lifetime. It is known that CdO is one of the most toxic substances being emitted into the environment in form of vapors by burning during exploitation. This is the main reason for as completely as possible replacement of CdO by other MeO like ZnO or SnO_2 [3]. However, in some cases, such as the contactors of I_n < 100 A, the known compositions with Ag-SnO_2 and Ag-ZnO are unable to reach the high-grade functional properties of Ag-CdO electrical contact materials [4, 5]. This is due mainly to the different thermodynamic characteristics of SnO_2 and ZnO compared to those of CdO, which is considered the ideal oxide for the quenching of the electric arc formed by the short-circuit currents [1].

In this paper there are presented the research results concerning the obtaining and physical-mechanical, characterization of some new Ag-ZnO and Ag-SnO_2 advanced sintered electrical contact materials with a uniform distribution of the reinforcing phase (MeO) that assures a low and uniform erosion degree, a high resistance to welding and a high electric arc quenching ability. These materials are presented comparatively with the classical Ag-CdO one of the same oxide phase content.

2. Experimental

The powder mixtures for the new contact materials with 90 wt. % Ag and 10 wt. % MeO (MeO = CdO, ZnO or SnO_2) were obtained by two methods:

- mechanical mixing;
- chemical precipitation.

The mechanical powder mixtures (MM) were prepared by dry homogenization of very fine powders of Ag and MeO type in a steel ball rotary mixer for 4 hours, in the following conditions:

- material/steel balls weight ratio: 1:1;
- steel balls diameter: 10 mm;
- degree of the mixing bowl volume filling: 80 %;
- bowl rotating speed: 40 r.p.m.

Then the (MM) powders were passed through a sieve with the sieve opening of 63 μm.

The chemical powder mixtures (CM) were prepared through a wet way by Ag precipitation from an aqueous solution of $Na_2CO_3 \cdot 10H_2O$, which was used as a precipitant. The Ag_2CO_3 precipitate was formed first “in situ“ from an $AgNO_3$ aqueous solution that contained a suspension of MeO particles, according to the chemical equation no. (1). The rate of the reactant dropping was of 40...60 ml/min, and the solution was strongly stirred with a rotation speed of 1500 r.p.m. for 2...4 hours. The working temperature was in the range of 20…40 °C. The MeO particles were not involved in reaction, remaining in suspension, in mixture with the new formed Ag_2CO_3. After that, the precipitates were filtered, dried at 100 °C for 2 hours, calcined in air at 450…550 °C for 2…4 hours to completely decompose the precipitated silver compounds in order to obtain the final Ag-MeO powder mixtures. At calcination, the decomposition reactions are described by the equations no. (2) and (3). For impurities removing, the (CM) powders were washed with distilled water. Subsequently, the (CM) powders were dried in vacuum at 100 °C for 2 hours.

$$2\ AgNO_3 + Na_2CO_3 = Ag_2CO_3 + 2\ NaNO_3 \qquad (1)$$

$$Ag_2CO_3 \rightarrow Ag_2O + CO_2 \qquad (2)$$

$$Ag_2O \rightarrow 2\ Ag + \tfrac{1}{2}\ O_2 \qquad (3)$$

The final (MM) and (CM) electrical contact materials were processed by powder metallurgy techniques, as follows:

- granulation of powder mixtures by pressing in blocks, their crushing, and separation by sieving of the agglomerated particle with the size within the range of 125…250 μm;
- pressing of the samples with a pressure of 300 MPa, in a steel die of appropriate shape and dimensions, into two-layers (one of Ag for brazing on the copper supports and one of Ag-MeO as contact material);
- sintering of the compacts in air at the final temperature of 850 °C for 4 hours, with a heat rate of 3…5 °C/min;
- re-pressing of the sintered compacts to the final shape and dimensions in a closed steel die, using a pressure of 1000 MPa.

Both the initial Ag and MeO powders, and (MM) and (CM) final powders were characterized from the density, particle size and flow rate point of view.

All the contact materials were characterized, in each processing step, by determining their main physical and mechanical properties. The microstructure was studied with an optical microscope directly on the polished un-etched final electrical contacts.

The functional tests were carried out according to the international standard IEC 947–4–1:1992 [13]. The electrical contact pieces were mounted in three electromagnetic contactors of $I_n = 40$ A for each type of electrical contact material, working in air in AC3 regime. Each contactor was equipped with six electrical contact pairs consisting of six pieces and six counter-pieces. The main functional characteristics (making and breaking capacity performed for 50 maneuvering cycles, and conventional service working performed for 6000 manoeuvering cycles.) have been determined on a proper testing stand.

3. Results and discussion

In Table 1, respectively Table 2 are presented the main physical properties and particle characteristics of the Ag and MeO powders, respectively of the Ag-MeO (MM) and (CM) powder mixtures, where ρ_t is the theoretical density of powder material, ρ_a is the apparent density of powder, d_{FSSS} (Fisher Sub Sieve Size diameter) is the particle mean diameter, d_{max} is the particle maximum diameter, and V is the flow rate of powder.

Table 1. The main physical properties and particle characteristics of the initial Ag and MeO powders.

Powder type	Purity, [%]	Melting point [°C]	ρ_t [g/cm^3]	ρ_a [g/cm^3]	d_{FSSS} [μm]	d_{max} [μm]
Ag	min. 99.9	961	10.50	1.70	4	32
CdO∗	min. 99.0	900	6.95	0.52	0.51	5
ZnO	min. 99.5	1975	5.47	0.41	0.49	5
SnO$_2$	min. 99.0	1127	6.93	0.38	1	5

∗CdO begin to sublimate from 700 °C slowly and from 900 °C intensively

Since the as obtained (MM) and (CM) powder mixtures do not flow due to their irregular particle shape and too small particle diameter, for their using on the automatic presses, it was necessary to granulate them. Both the powders nature and the particles size influence the flow rate of the powders. Therefore, the flow rate of the (MM) coarser powders is better than of the (CM) very fine powders.

Table 2. Theoretical density and the main particle characteristics of the obtained Ag-MeO (MM) and (CM) powders.

Material type	ρ_t [g/cm^3]	n.g.p.	g.p.*		d_{FSSS} [μm]	d_{max} [μm]
		ρ_a [g/cm^3]	ρ_a [g/cm^3]	V [s/50g]		
Ag-CdO (MM)	9.989	2.54	2.91	8	3.46	32
Ag-ZnO (MM)	9.616	2.47	2.87	7	3.43	32
Ag-SnO$_2$ (MM)	9.986	2.36	2.83	7	3.50	32
Ag-CdO (CM)	9.989	1.42	2.59	9	0.84	5
Ag-ZnO (CM)	9.616	1.39	2.53	9	0.76	5
Ag-SnO$_2$ (CM)	9.986	1.34	2.44	10	1.30	5

Note: n.g.p.–non-grained powder,
g.p.*–granulated powder

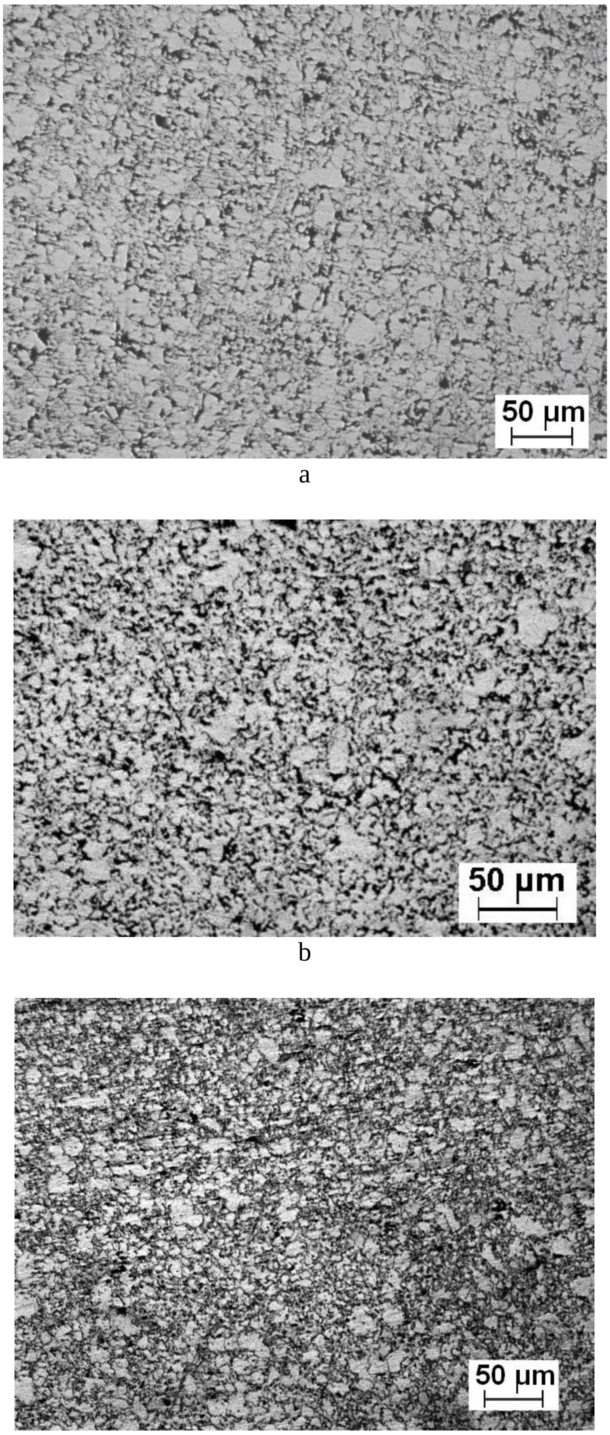
The main physical - mechanical characteristics of the Ag-MeO 90-10 (MM) and (CM) final contact materials are presented in table 3.

Table 3. The main physical - mechanical characteristics of the Ag-MeO (MM) and (CM) final materials.

Material type /material no.	Final density, ρ_f [g/cm^3]	Relative density, ρ_r [%]	Hardness HB (hard)	Resistivity [μΩ·cm]
Ag-CdO (MM)/(1)	9.42	94.31	82	2.4
Ag-ZnO (MM)/(2)	9.06	94.22	84	2.5
Ag-SnO$_2$ (MM)/(3)	9.40	94.13	87	2.7
Ag-CdO (CM)/(4)	9.55	95.61	94	2.3
Ag-ZnO (CM)/(5)	9.19	95.57	97	2.4
Ag-SnO$_2$ (CM)/(6)	9.53	95.43	103	2.6

As it is observed in Table 3, the physical and mechanical properties of the Ag-MeO materials processed from (MM) powders are inferior to those obtained from (CM) powders. The sintering occurs in the solid state for all types of materials, but in the case of the (CM) powders due to the very high specific surface it is obtained a higher relative density, especially for the Ag-CdO material. Also, the (CM) materials present a higher hardening by dispersion comparatively with the (MM) ones.

In Fig. 1, respectively Fig. 2, there are shown the microstructures of the Ag-MeO (MM), respectively (CM) materials.



a

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Fig. 1. Microstructures of the Ag-MeO (MM) materials:
a) MeO = CdO, b) MeO = ZnO, c) MeO = SnO_2.

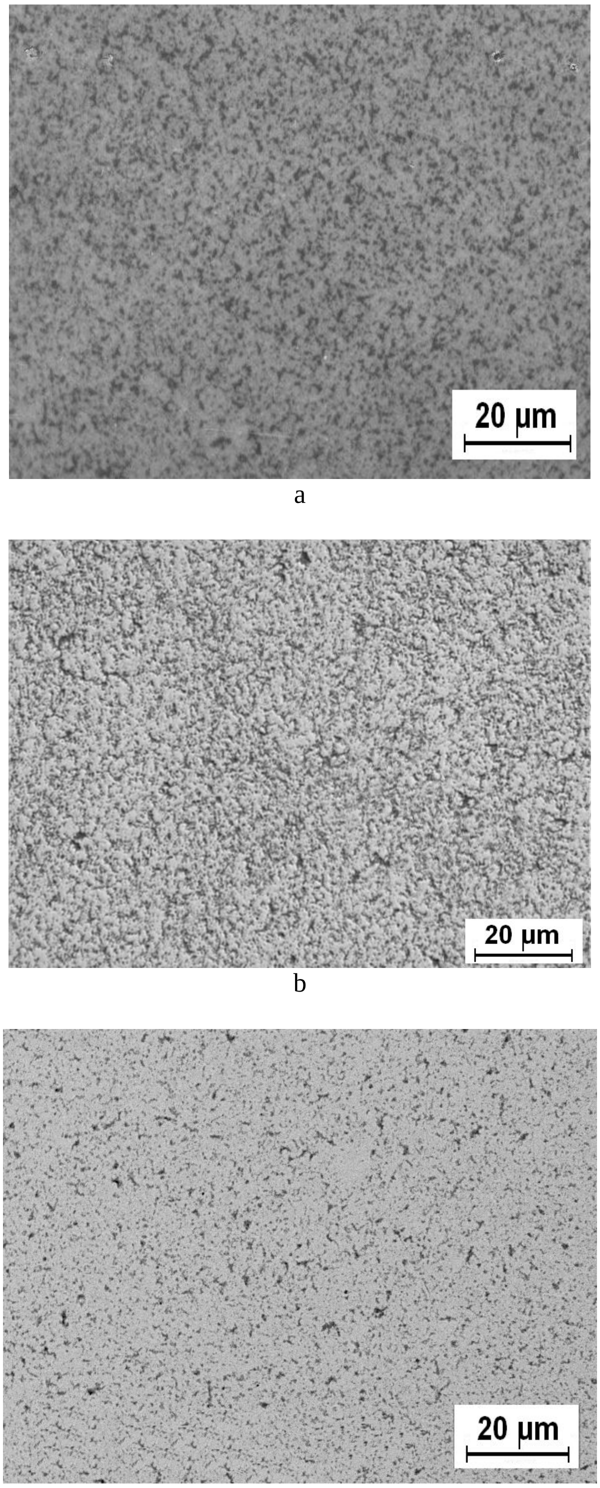

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Fig. 2. Microstructures of the Ag-MeO (CM) materials:
a) MeO = CdO, b) MeO = ZnO, c) MeO = SnO_2.

As can be seen in Fig. 1 and Fig. 2, the (MM) and (CM) final materials have fine and uniform dispersions of the MeO in the Ag matrix, but the electrical contacts obtained from (CM) powders are superior to those from (MM) ones. It is known that the microstructure influences directly the functional behavior of the contact materials [14].

The results of the making and breaking capacity, and conventional service working tests are presented in Table 4 and table 5, respectively.

Table 4. The results of the making and breaking capacity tests.

Specific parameters	Making and breaking capacity						
	Imposed values	Measured values/material no.					
		(1)	(2)	(3)	(4)	(5)	(6)
Remaking voltage at 50 Hz [V]	420… 483	434	420	423	437	422	425
Making and breaking current [A]	296… 340	329	318	323	331	320	325
Cos φ	0.4…0.5	0.40	0.40	0.40	0.50	0.50	0.45
Passing current duration [s]	~ 0.05	0.04	0.04	0.04	0.04	0.04	0.04
Break duration [s]	30	30	30	30	30	30	30
Oscillation frequency [kHz]	93.06… 113.7	94.98	93.38	93.45	95.41	93.53	93.96
Over oscillation factor	1.05… 1.15	1.11	1.08	1.09	1.12	1.09	1.10

Table 5. The results of the conventional service working tests.

Specific parameters	**Conventional service working**						
	Imposed values	**Measured values/material no.**					
		(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**
Remaking voltage at 50 Hz [V]	420… 483	430	416	419	432	418	420
Making and breaking current [A]	74… 85	79	74	74	81	75	75
Cos φ	0.4…0.5	0.49	0.46	0.48	0.50	0.47	0.49
Passing current duration [s]	~ 0.05	0.05	0.04	0.05	0.05	0.04	0.06
Break duration [s]	10	10	10	10	10	10	10

The acceptance criteria imposed in the standard in force [13] for the electrical contact pieces regarding to the no forming of permanent electric arc, electric arc striking between the poles and welding of the contact pieces during the tests, were fulfilled wholly of all types of materials.

Tables 4 and 5 show some closed data regarding to the functional behavior of the six types of materials.

The electrical erosion visible with the naked eye, for the Ag-SnO_2 (CM) and (MM) and Ag-ZnO (CM) and (MM) is more uniform comparatively with the Ag-CdO (CM) and (MM), as a result of the differences between the thermodynamic characteristics of the SnO_2 and ZnO, and CdO respectively, which in turn lead to some differences between the electrical erosion mechanisms. The CdO sublimates intensively beginning with the 900 °C (see Table 1). The electric arc is quenched by the absorbed heat of CdO for its sublimation. The CdO is dissipated in the environment, while the SnO_2 and ZnO remain on the electrical contact surface increasing viscosity of the Ag-MeO melting, and as a result it leads to more uniform erosion comparatively with the Ag-CdO materials.

In the same time, a visible difference appeared between electrical erosion of the types of (MM) and (CM) materials due to the differences between their microstructures. The (CM) materials present a higher degree of MeO particle dispersion and uniformity in the silver matrix, as well as a lower porosity and a higher hardness comparatively with the (MM) materials.

The electrical contact surfaces of all types of materials present some microscopic cracks, melted drops and holes at the end of the tests.

4. Conclusions

The functional test results presented in this comparative study concerning the Ag-MeO (MeO = CdO, ZnO or SnO_2) contact materials behaviour in electromagnetic contactors of I_n = 40 A have proved that all the studied materials fulfilled the acceptance criteria imposed in the standard in force for the electrical contact pieces.

However, as a result of the differences between the processing methods and the nature of the MeO powders, which in turn led to differences among the porosity, hardness, resistivity, microstructure, only some minor differences upon the electrical erosion were noticed.

So, the (CM) materials presented a higher degree of MeO particle dispersion and uniformity in the silver matrix, as well as a lower porosity and a higher hardness comparatively with the (MM) materials.

The electrical erosion of the Ag-SnO_2 (CM) and (MM) and Ag-ZnO (CM) and (MM) is more uniform comparatively with the Ag-CdO (CM) and (MM), due to the differences between the thermodynamic characteristics of the MeO. Also, the electrical erosion of the (CM) materials is better than the (MM) ones due to their higher degree of MeO particle dispersion and uniformity in the Ag matrix, as well as due to their lower porosity and higher hardness.

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