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# New WAg electrical contacts with ultrafine structure for low voltage devices

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The paper presents the research results concerning the obtaining of a new type of WAg sintered electrical contacts with a high silver content for safety switches working in air up to 500 A. The applied method is based on powder metallurgy techniques. This method starts with powder mixtures manufacturing by chemical coprecipitation of $AgWO_4$ from aqueous solutions, the precipitate processing by reducing in a $H_2$ stream to a very homogenous and fine dispersed WAg powder mixture and final electrical contact pieces obtaining by pressing, sintering and reshaping. The technological parameters, as well as to the characterization of the obtained powders and sintered electrical contacts are presented. The new electrical contacts present a very fine microstructure, and as a result, they have some improved physical, mechanical, electrical and functional characteristics.

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*Keywords*: Fine microstructure, Tungsten silver, Electrical contacts

## 1. Introduction

The tungsten based pseudoalloys, of W/WC - Ag/Cu type, are some of the most used materials for the electrical contacts of the breaking devices, responding very well to requirements related to arc interrupting capabilities, erosion and welding and satisfactory to contact resistance. The applications of these materials were extended in a broad series of devices to protect of high short-circuit currents and where resistance to erosion by high current arc is very important.

In the circumstance, in which the principles of arc quenching in electrical devices remained not changed, some improved materials are necessary to be obtained in order to allow the interruption of default currents without important material erosion, contact deformation or welding. In the last time, a lot of works were developed to improve the functional characteristics by achieving of some uniform and fine dispersion microstructures, simultaneously, with a high compacting rate [1 - 12].

Also, recently works of G. Rener and U. Siefken [13], show that very fine W powders, having an average grain size of at most 2 µm, preferably 0.01 to 1 µm, may be more easily processed by mechanical homogenization with Ag powder, sintering and reshaping by inductive heating, extrusion, rolling or forging. By this method, a very high rate of compacting (min. 99.5 %) is obtained.

The paper presents the research results concerning the obtaining of some new WAgNi sintered electrical contacts with improved microstructure starting from some uniform and ultra fine dispersed powder mixtures manufactured by chemical precipitation. The new materials are presented comparatively, with some materials obtained by mechanical homogenization. These types of electrical contacts are suitable for safety switches.

## 2. Experimental

The contribution of our work consists of obtaining of some very uniform and ultra fine dispersed powder mixtures by the methods of W, Ag and Ni chemical coprecipitation at neutral pH, from $Na_2WO_4$ + $AgNO_3$ + $Ni(NO_3)_2$ solutions, and their processing in form of electrical contacts by powder metallurgy techniques.

The $Na_2WO_4 \cdot 2H_2O$, $AgNO_3$ and $Ni(NO_3)_2 \cdot 6H_2O$, as well as W, Ag and Ni powders were obtained by recovering from WCo sintered hard pseudoalloy scrapes and AgNi electrical contact scrape, using the well known chemical processing [14].

The amounts of the recovered raw materials were calculated to obtain the chemical compositions according to the stoichiometry of forming reactions of $Ag_2WO_4$ and $Ag_2WO_4$ + $NiWO_4$ precipitates, respectively.

The metals were precipitated from solutions simultaneously, in form of $Ag_2WO_4$ + $NiWO_4$ insoluble mixtures, which were purified, dried and reduced in a dry $H_2$ stream having a dew point of 40 ºC and a flow rate of 120…200 l/hour.

The reduction reaction was carried out on thin layers of material, in two steps, at 200…300 ºC and 700…900 ºC, each for 1 hour. In the reduction process we used two steps in order to avoid the increase of tungsten grains and silver segregation. After reduction, all types of above presented powders were passed through a sieve with the mesh size of 63 µm.

Also, some classical mechanical mixtures of W, Ag and Ni recovered powders having the same chemical composition were prepared in order to realize a comparative study regarding the influence of grain size and powder manufacture method upon the electrical contact characteristics. The mixtures were homogenized for 2 hours, in a proper mixer, to avoid the oxidation of the powders.

All the new types of WAgNi powder mixtures were processed according to the well known techniques of powder metallurgy: pressing of the powder mixtures at 200…1200 MPa in form of porous plates, sintering in liquid phase for 2…4 hours at 600 ºC; 700 ºC; 800 ºC; 850 ºC and 900 ºC and repressed at 1200…1500 MPa.

Following the route of the technological flow, the products were characterized from chemical, grain size, morphological, mechanical, electrical and functional point of view.

*The chemical composition* was assayed by standard gravimetric analysis.

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

*The bulk density* was determined in standard conditions, by sample weight measuring and rating to its specific volume.

*The morphological aspect* was analyzed by optical microscopy, using a Carl Zeiss optical microscope of NU 2 type.

*Microstructure analyzes were carried out* on etched samples with a Nital solution.

*The grain size distribution* was measured using a Mettler settling balance of SB type, by graphically recording of the powder weight variation in time, as a result of particles settling, according to Stokes law. Previously, the powder was dispersed by ultrasounds, in an aqueous solution of 1 wt. % sodium pyrophosphate.

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

*The electrical conductivity,* was directly measured at room temperature with a SIGMASCOP - EX 8 device.

*The functional tests* were performed on especial stands for the behavior testing of electric devices, using the safety switches fitted with cylindrical electrical contacts (fixed contacts: flat, Φ = 6 mm, h = 5 mm, and movable contact: 15 mm spherical radius, Φ = 6 mm and h = 5 mm) according to the international standard CEI 947 – 2 – 1989. A circuit breaker for the intermediate voltage range has to stand at least 10000 operations at rated current, and at least 30 operations in short circuit cases [15].

*The contact resistance* tests, as function of silver content and switching number, at $I_n$ = 350 A and $I_n$ = 1000 A, were carried out for a closing/opening velocity of 7 cm/s and a closing/opening force of 30 N. The measurements were made at every hundred operations. The test ended at 1000 operations.

*The voltage drop* tests at $I_n$ = 50 A were performed on a relay, with a tungsten lamp, and 60 Hz, energized sequentially by a motor cam drive, at a rate of six times per minute, with an on-time of 1 s. The changes of the contact surface resistance, as a function of operating life (8000 operations interrupted after each 1000 operations for measurements) were measured at a closing/opening velocity of 7 cm/s and a closing/opening force of 15 N.

*The weight loss*, as a function of switching number, were performed on the same device of voltage drop test, at $I_n$ = 50 A, by measuring of difference between starting electrical contact weight and its weight, after each series of 2000 operations.

*The weld behavior*, was tested during of 1000 cycles, carried out on symmetrical pairs of electrical contacts, as a function of force required to detach the welded electrical contacts in arcing current, in the followed conditions: I = 1300 A, closing/opening velocity of 100 cm/s, contact force of 60 N. Because the measuring results are dispersed in some large ranges, usually, the cumulative probability distribution of weld strengths as a function of welding force is presented.

## 3. Results and discussion

Table 1 presents the compositions of the WAgNi chemical powder mixtures (CM), WAgNi mechanical powder mixtures (MM) and W, Ag and Ni recovered powders (R). As it can be observed, the chemical compositions of the powders mixtures and of the W, Ag and Ni recovered powders correspond to the used powders in the common manufacturing methods of the electrical contacts.

Average grain size, $d_{FSSS}$, specific surface, bulk density and weight loss of the recovered powders and powder mixtures are presented in Table. 2.

*Table. 1. Chemical composition of the powder mixtures used for the WAgNi electrical contact manufacture.*

| Type of the powder mixture and recovered powder | Chemical composition, wt. % | | | | | |
|---|---|---|---|---|---|---|
| | Theoretical | | | Realized | | |
| | W | Ag | Ni | W | Ag | Ni |
| WAgNi – CM | 45.54 | 53.45 | 1.00 | 46.05 | 52.90 | 1.05 |
| WAgNi – MM | 45.54 | 53.45 | 1.00 | 45.60 | 53.43 | 0.97 |
| W - R | - | - | - | min. 99.5 | - | - |
| Ag - R | - | - | - | - | min. 99.9 | - |
| Ni - R | - | - | - | - | - | min. 99.6 |

*Table 2. Average grain size, $d_{FSSS}$, specific surface, bulk density and weight loss of the recovered powders and powder mixtures.*

| No. of sample | Name and type of powders or powder mixtures | $d_{FSSS}$, µm | Specific surface, $m^2/g$ | Bulk. density $g/cm^3$ | Weight loss, wt. % | |
|---|---|---|---|---|---|---|
| | | | | | $H_2O$ | O |
| 1 | Ag - R | 2.5 | 0.9 | 1.8 | 0.01 | 0.001 |
| 2 | W - R | 1.4 | 0.8 | 2.3 | 0.05 | 0.3 |
| 3 | Ni - R | 1.8 | 0.4 | 1.1 | 0.01 | 0.01 |
| 4 | WAgNi - CM | 0.5 | 3.7 | 1.6 | 0.05 | 0.3 |
| 5 | WAgNi - MM | 1.9 | 0.8 | 2.0 | 0.01 | 0.01 |

Weight loss is referred to as “loss on reduction” (LR) carried out in a $H_2$ stream. LR at 120 ºC for 1 hour represents $H_2O$ content, and LR at 900 ºC minus LR at 120 ºC represents $O_2$ content.

Fig. 1 presents the morphological aspects of the powders used for electrical contacts. The W powder presented in Fig. 1 (a) was obtained by complete reduction of monoclinic ammonium paratungstate, in two stages, at temperatures of 300 ºC and 900 ºC, respectively. The particles developed well-defined facets at this temperature, especially by holding at temperature for a prolonged period after the completion of oxide reduction. The recrystallized particles retained within the framework of the original material. The Ag powder presented in Fig. 1 (b) was obtained by electrochemical purification and as a result the particles have a specific dendritic shape. The WAgNi - CM powder mixtures, presented in Fig. 1 (c) was obtained by hydrogen reduction, in two stages, at 300 ºC and 900 ºC, of the $Ag_2WO_4$ + $NiWO_4$ chemical coprecipitated mixture. The particles are very fine and uniform dispersed. The W and Ag particles are indistinguishable practically. Fig. 2 presents the particle size distribution of the W, Ag and WAgNi - CM powders.

The W powder is included in the category type of fine powders and Ag powder in the medium ones. The WAgNi - CM powder mixture is included in the category type of ultra fine powders.

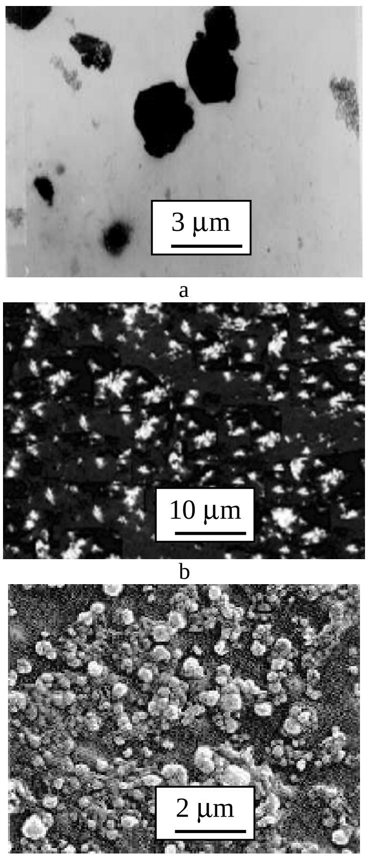



*Fig. 1. Morphological aspects of W powder (a), Ag powder (b) and WAgNi - CM powder mixtures (c).*

In the powder mixtures, which were obtained either by chemical or mechanical homogenization, the components are uniformly and finely dispersed. The W particle size is controlled by the temperature of the second step of tungstate powder reduction. Lower temperatures lead to finer W particles, all of sub micrometer size, but temperatures of 850…900 ºC are necessary to achieve a complete reduction and a material easy to handle. In the same time, the grain size increases to 1 µm. The complete reduced W particles are finer as Ag particles that appear more spherical. However, W particles are hardly distinguished from the Ag ones.

Fig. 3 shows the variation of green density and sintering density versus compacting pressure and sintering temperature of WAgNi - CM powders.

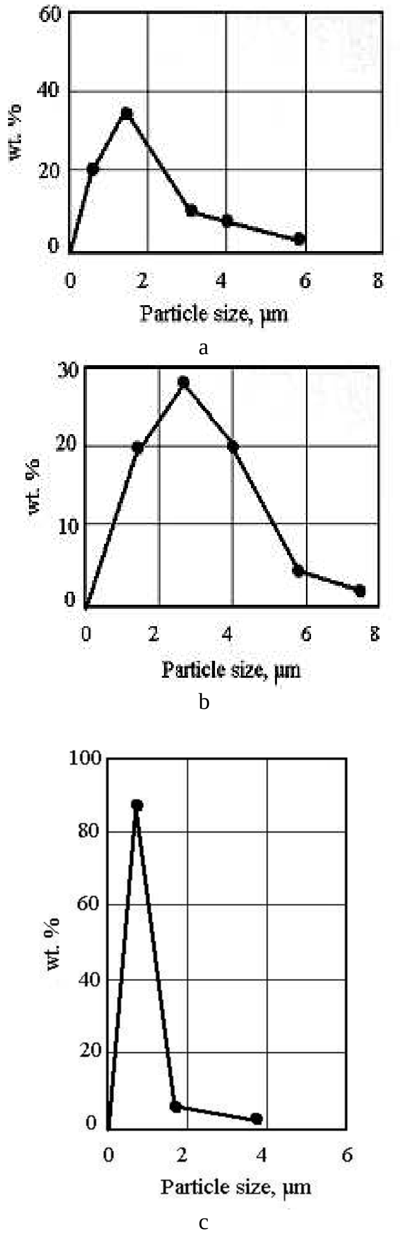



*Fig. 2. Grain size distribution of: W powder (a), Ag powder (b) and WAgNi – CM powder mixtures (c).*

The mechanical powder mixtures have an improved pressability similar with the chemical ones. On the other hand, the sinterability is slightly lower. These differences change in the range of 3….5 %.

It is very clear that a compacting pressure of over 600 MPa, preferably of 900 MPa is necessary to break up the agglomerates from nickel doped powders in order to yield an acceptable green densities. By sintering at 750 ºC a low degree of shrinkage appears, while at 950 ºC segregations of silver to the lower side of the pieces occurred, causing sample deformation. The best compacting degree is obtained by sintering at 850 ºC for 2 hours.

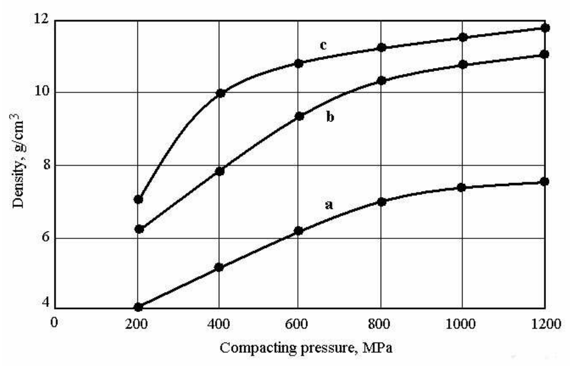



*Fig. 3. The green density (a), and the sintering density (b, c) of WAgNi - CM powders: the sintering conditions: b -700 ºC for 2 hours, and c – 800 ºC for 2 hours.*

Table 3 presents the main characteristics of the new electrical contact materials obtained after repressing at 1200 MPa.

*Table 3. Physical and electrical characteristics of the WAgNi electrical contact materials.*

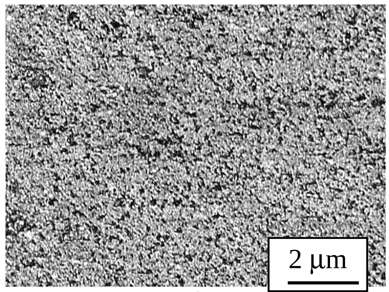
| Name of electrical contact material | Density, $g/cm^3$ | | Hardness, HV10 | Electrical conductivity, $m/\Omega.mm^2$ |
|---|---|---|---|---|
| | Achieved | Theoretical | | |
| WAgNi - CM | 11.98 | 13.25 | 170…180 | 26 |
| WAgNi - MM | 12.80 | 13.27 | 170…175 | 25 |

The relative density of the material from chemical powder mixture is of 90.42 %. The compacting rate of the material from mechanical mixture is of 96.46 %.

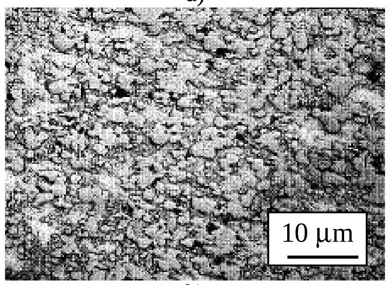
According to the results of G. Renner [13], merely by a subsequent hot extrusion, forging or rolling of the WAgNi sintered materials having ultra fine dispersed W particles in a Ag matrix is possible to obtain some composites with a residual porosity of less 0.5 %.

Thereof, our materials with a residual porosity of 9.59 % and 3.55 %, respectively, were subjected to an induction heating and heating state forging. As a result, for the both samples the residual porosity was decreased below 0.5 %.

Fig. 4 presents comparatively the optical microstructure of the WAgNi - CM and WAgNi – MM electrical contact materials.




a)




b)

*Fig. 4. The optical microstructures of the WAgNi – CM (a) and WAgNi – MM (b) electrical contact materials.*

The microstructures presented in Fig. 4 show some materials having an ultra fine and fine dispersion of sub micrometer and micrometer W particles in the Ag matrix. As can be seen, there is a low content of pores being visible as dark areas on the etched electrical contact surface. These are very fine and uniformly dispersed in the material. Because the Nital solution etched the material at the grain boundary it is possible to observe the shape of the tungsten particles. It is observed that by sintering a minor change in microstructure occurred. The W particle size and distribution remained constantly. There are not observed agglomerates of W or Ag particles.

The functional tests were carried out relative to contact resistance, voltage drop, weight loss by electrical erosion and welding resistance. The obtained values, below presented for WAgNi – CM, are slightly improved (about 3…10 %) in respect with the WAgNi – MM material, as Fig. 5…10 show.

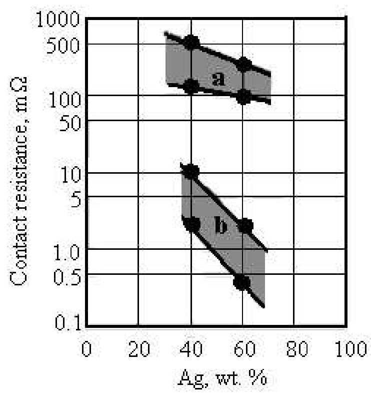



*Fig. 5. Contact resistance of WAgNi – CM electrical contacts, as a function of Ag content: $I_n$ = 350 A (a) and $I_n$ = 1000 A (b).*

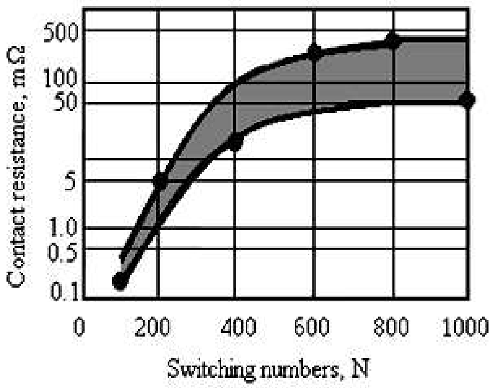



*Fig. 6. Contact resistance of WAgNi –CM electrical contacts as a function of switching numbers , N, at $I_n$ = 350 A.*

As a result of current switching and continuous arc erosion, the *contact resistance* increases by $WO_3$ and $Ag_2WO_4$ non-metallic layers formation on the surface of the electrical contacts. $WO_3$ has semiconducting properties (n-conducting).

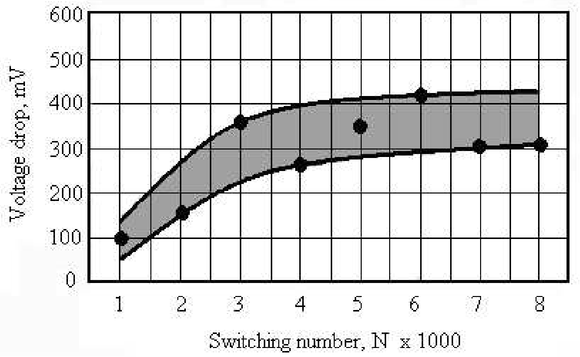



*Fig. 7. Voltage drop of WAgNi – CM electrical contacts as a function of switching numbers, N, at $I_n$ = 50 A.*

As we can see from Fig. 5…7, the resistance of surface layers is strongly dependent on the measuring current. At small currents, the resistance is nearly independent of arc current. In the beginning of the tests, the contact resistance had low values (under 0.5 mΩ). After a few hundred of switching, the contact resistance increases very much. After that, depending of the current value it reaches a nearly stationary scattering range. Fig. 5 shows that the contact resistance decreases with the increasing of the Ag content and the nominal current. Also, Fig. 7 shows that the voltage drop increases to a number of closings and then it increases very slowly. These observations are valid for the both type of materials.

Because of a large distribution of measuring points, a direct comparison of the examined materials is difficult. However, we can assert that the contact resistances of the WAgNi - CM material and the WAgNi - MM material are very close.

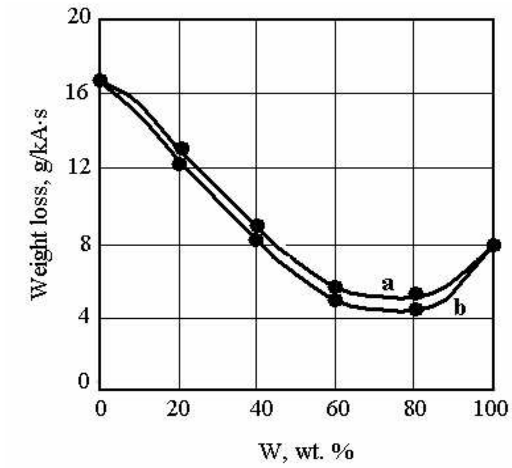



*Fig. 8. Weight loss as a function of W content: a) WAgNi – MM electrical contacts, b) WAgNi – CM electrical contacts.*

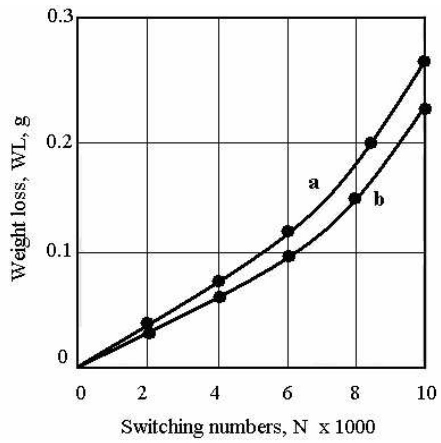



*Fig. 9. Weight loss, WL, as a function of switching numbers, N: WAgNi - MM (a) and WAgNi - CM (b).*

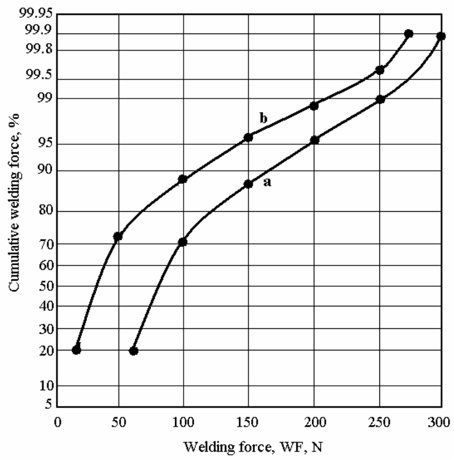



*Fig. 10. Cumulative welding force, WF, at I = 1300 A: WAgNi - MM (a) and WAgNi - CM (b).*

As can be seen in Fig. 8 and Fig. 9, the electrical erosion of the both materials depends more on the chemical composition than on the microstructure. The electrical erosion resistance of the WAgNi - CM material is better than WAgNi - MM material for all kind of compositions because the W and Ag particles have some very fine grain sizes and these are very uniformly dispersed. In addition, the high degree of compaction improves arc erosion properties. However, extension of the fineness of W particles dispersions to a very high level may lead to a catastrophic failure in electrical erosion behavior. The weld tests, presented in Fig. 10, show that WAgNi – MM materials have a behavior slight improved than the WAgNi - CM materials because the low-density electrical contact materials tend to weld less than the high-density as a result of porous structure. Therefore, the welded areas of the surface break away more readily.

The general results of the functional tests show that the new kind of electrical materials have slightly improved properties comparatively with the commercially ones.

## 4. Conclusions

The works were carried out based on the finding that by using a very fine-grained W powder, a high degree of compacting (> 99.5%) can be achieved by a suitable reshaping made after sintering. This is possible due to the higher values of shrinkage at sintering of fine-grained W powders as the coarse-grained ones.

According to the proposed method, the new materials for electrical contacts having superior physical, mechanical and structural characteristics achieve some high functional characteristics concerning the contact resistance and arc erosion, too.

So, the paper approached two very important problems:

- *the first*, of scientific interest, concerning the obtaining of some new AgW electrical contact materials starting from ultra fine and uniform dispersed powder mixtures obtained by chemical precipitation and mechanical homogenization;
- *the second*, of technical - economical interest, concerning the recycling of scrapes of hard pseudoalloys on WCo basis and of electrical contact pieces on the Ag basis, respectively, in form of a new kind of electrical contact material.

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