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NANOCRYSTALLINE Ag-Re COMPOSITE AS A POTENTIAL MATERIAL FOR ELECTRIC CONTACTS FABRICATION

A new silver-based composite material with an addition of 1 and 10 mass % of rhenium, for prospective application in the production of electric contacts, has been presented. The paper shows results of the research and experimental works aimed at developing technology for fabrication of semiproducts (wires and bimetallic contacts) by classical powder metallurgy methods and by a method enabling production of nanocrystalline composite. At each stage of the processes involved, physical, mechanical and technological properties of the materials were investigated. Particular attention was given to final products and semiproducts prepared in a form of bimetallic contacts. It was found that the composite with nanocrystalline structure may be a good material for ecological electric contacts.

Keywords: electric contact; composite; nanocrystalline; contact materials; arc erosion; examination methods; electric properties

1. Introduction

Up to the present, the use of rhenium in the production of contact materials was very limited for two reasons. Firstly, the price of this element is very high, and secondly, rhenium exhibits an ability to forms Re2O7 oxide characterized by a melting point of 569K and boiling point of 635K [1]. This behaviour results in undesired loss of mass of contact materials due to erosive action of an electric arc, while on the other hand, these contacts exhibit high tacking resistance [2]. There are several literature reports on mostly successful application of rhenium in contact materials [3-5]. However, this element is generally not used as a component of these materials except for some of application in external motors of boats, where its high resistance to the effects of sea water was taken into account [6]. Over the last few years, the research on application of rhenium in the production of contact materials has been conducted at the Institute of Non-Ferrous Metals in Gliwice [7-13]. The aim of some of works carried out was to develop new-generation AgRe-type nanocrystalline materials using high-energy milling and suitably conducted plastic consolidation. This paper summarizes the results obtained from these works, related mainly to fabrication technology and preliminary examination of the physical, mechanical and electric properties of these novel materials.

2. Experimental

2.1. Materials

The starting materials for this research were metallic powders of silver and rhenium. The Ag powder was obtained by water atomization, and rhenium powder was prepared by reduction of ammonium perrhenate by hydrogen. The median particle size of the silver and rhenium powders used to fabricate composites by classical powder metallurgy methods was 28 and 1 μm, respectively. In case of the composites made by high-energy milling, the median particle size for Ag and Re was 22μm and 2μm, respectively. The particle size distribution was determined by a laser method. Fig. 1 shows morphology of both powders, confirming considerable difference in the size of particles of silver and rhenium. Some of the Ag particles are sphere-like shaped, whereas the others are irregular in shape. Morphology examination of the metallic rhenium powder showed that its particles are very small and irregular in shape.

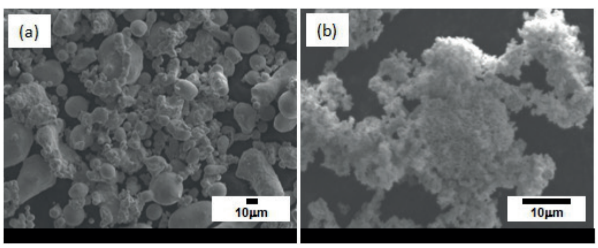

Fig. 1. Morphology of the powders of: (a) silver, magnification 500×, (b) rhenium, magnification 2000×

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2.2. Preparation of sample batches of the Ag-Re contacts

2.2.1 The AgRe10 composite fabricated by classical powder metallurgy

The Ag 90% and Re 10% (in mass %) composition was selected for fabrication of the Ag-Re composite contact. In order to homogenize chemical composition, the metal powders were subjected to mixing. The mixtures were consolidated into compacts, about 18 mm in diameter, using an isostatic press with specially-made elastic moulds, and then sintered in a vacuum furnace. Next, the compacts were subjected to extrusion using a hydraulic press operating under the KOBO system (Fig. 2) at the extrusion ratio λ=20, followed by consolidation by drawing and heat treatment. Finally, the contacts were fabricated as a final product using horizontal upsetting machines. In this process of contact rivets production, it is necessary to perform an additional operation of diffusive annealing so as to ensure metallurgical connection of a contact material with copper.

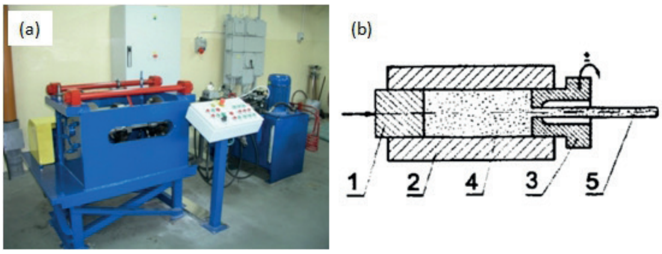

Fig. 2. The KOBO hydraulic extrusion press for extruding metals and alloys: (a) KOBO hydraulic press (b) diagram of the hydraulic press: 1 – punch, 2 – container, 3 – a die rotating on both sides, 4 – starting material, 5 – final product [14]

2.2.2 The AgRe10 nanocrystalline material

The tests started from preparation of the Ag-Re composite with the chemical composition Ag 90% and Re 10% (in mass %). Weighed amounts of both powders were subjected to mixing in order to homogenize chemical composition of the mixture, from which a reference sample was taken and analysed with respect to morphology, physical properties and phase content. The results obtained are shown in Fig. 3a and Table 1.

The milling operation was conducted under protective atmosphere of argon, with a drum rotary speed being gradually increased from 45 to 140 rpm. Physical properties of the AgRe10 composite powder were determined at each stage of processing. The obtained results are given in Table 1. The density and specific surface area of the powder composite decrease with the increase of process time, which can be related to the formation of the pores within the material volume and a change of the character of powder morphology from spherical to flaky. The shape of the particles at particular process stages is shown in Fig. 3. The change of crystallites' size depending of milling time was determined using a Scherrer method. It was found that size of silver crystallites decreases with increase of milling time (see Table I). The composite powder was then subjected to isostatic pressing into the compacts φ18mm in diameter, conducted in a special elastic mould. Next, these compacts were sintered in a hydrogen atmosphere and then subjected to extrusion by means of the KOBO hydraulic press (Fig. 2).

TABLE 1

Physical properties of a reference sample and the AgRe10 composite powder after high-energy milling

Milling time, hours	Drum rotary speed, rpm	Density, g/cm^3	Specific surface area, m^2/g	Size of Ag crystallites, nm
Reference sample	-	10.86	0.17	>200
31	45	10.74	0.10	142
150	140	10.57	0.07	86

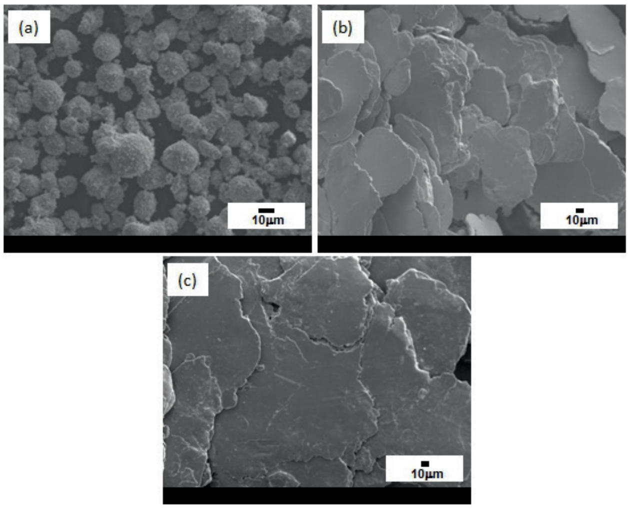

Fig. 3. Morphology of the AgRe10 powder: (a) reference sample, magnification 600×; (b) after 31 hours of milling, magnification 300×; (c) after 150 hours of milling, magnification 300×

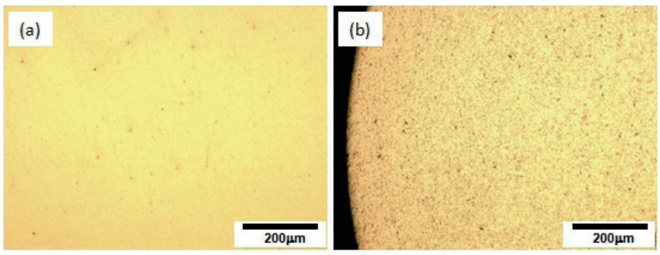

Fig. 4. Microstructure of a wire on its cross-section, magnification 200×: (a) AgRe1, (b) AgRe10

The composite was extruded into wire 2.5 mm in diameter, using an extrusion ratio λ=52. The obtained wires obtained were consolidated by drawing and heat treatment. Fig. 4b shows microstructure with clearly seen uniform dispersion of rhenium within a silver matrix.

Electric contacts as final products were manufactured similarly as the composite rivets made by classical powder metallurgy methods. The bimetallic rivets made from nanocrystalline AgRe10 material are presented in Fig. 5.

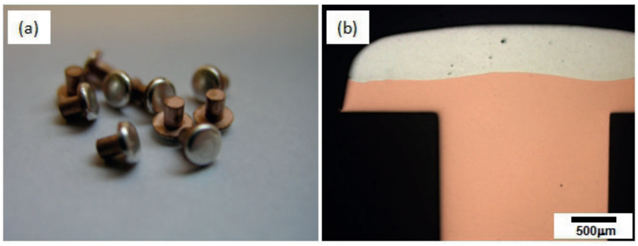

Fig. 5. Bimetallic contact rivets AgRe10/Cu 10BW4/1x2/2.5 (10 mm – radius of a head, B – bimetallic, W – convex, 4 mm – diameter of head, 1 mm – height of head, 2 mm – diameter of leg, 2,5 mm – height of leg): (a) rivets, (b) rivet cross-section

2.2.3 Nanocrystalline AgRe1 material

Under the work [10], the AgRe1 composite material has been fabricated. Suitable amounts of the powders of Ag 99% and Re 1% (in mass %) were mixed, and a sample was taken from the powder mixture. This reference sample was subjected to the examination of morphology, physical properties and to the XRD analysis. The obtained results are shown in Fig. 6a and Table 2.

The high-energy milling process was conducted under protective atmosphere of argon, with a drum rotary speed of 82 rpm. The results obtained are shown in Fig. 6b and Table 2.

TABLE 2

Physical properties of a reference sample and the AgRe1 composite powder after high-energy milling

Milling time, hours	Drum rotary speed, rpm	Density, g/cm^3	Specific surface area, m^2/g	Size of silver crystallites, nm
Reference sample	-	10.47	0.08	81*
30	82	10.39	0.03	42

* - size of crystallines of silver obtained after the atomization process

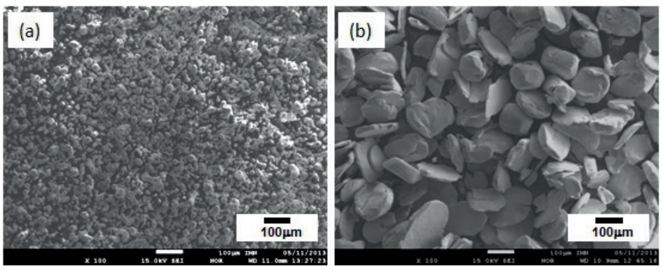

Fig. 6. Morphology of the AgRe1 powder, magnification 100×: (a) reference powder, (b) after 30 hours of milling

Next, the composite powder was subjected to two-sided compaction using a hydraulic press with steel dies. The compacts obtained, were then sintered in an hydrogen atmosphere and extruded by means of a hydraulic press operating under the KOBO system (Fig. 2). The extrusion ratio was λ=52, and the wire obtained was 2.5 mm in diameter. Microstructure of this wire is shown in Fig. 4a. It was used to fabricate bimetallic rivets AgRe1/Cu 10BW4/1x2/2.5, which were next subjected to heat treatment.

2.3. Examination of arc erosion resistance

The 10BW4/1x2/2,5 type contacts made from the materials compositions were subjected to the examination of arc erosion resistance at different currents: 10 A direct current and 60 A alternating current. The tests with DC current were conducted using an equipment shown in Fig. 7. Mechanical and electrical test parameters were presented in Table 3.

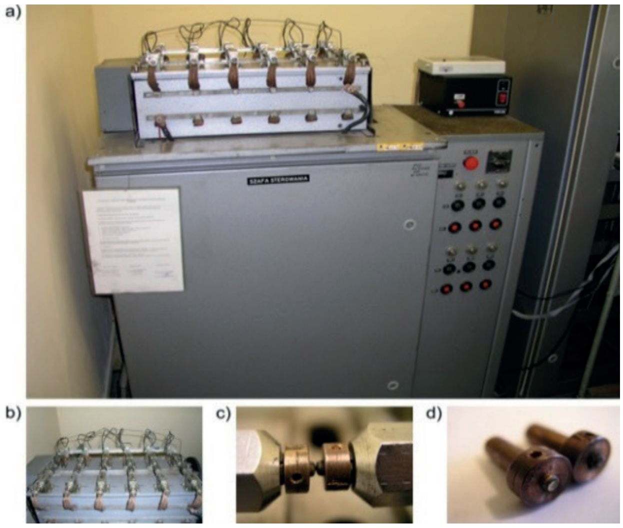

Fig. 7. Model equipment for the examination of arc erosion of the contacts: (a) measuring stand, (b) current circuits, (c) current circuit with a pair of contacts, (d) contacts with fixtures

TABLE 3

Electric and mechanical parameters of the arc erosion resistance tests

Parameter	Direct current, DC	Alternating current, AC
Current, A	10	60
Voltage, V	550	230
Distance between contacts, mm	6	5
Force of pressure, N	10	10
Number of switching cycles	50 000	15 000

The mass losses were also determined for the pairs of bimetallic contacts AgRe1/Cu, AgRe10/Cu, Ag(SnO_2)10/Cu and AgNi10/Cu.

In order to compare Ag-Re nanocrystalline material with other contact materials the similar contacts made from Ag(SnO_2)10 and AgNi10 were purchased in the external company.

Ag(SnO_2)10 was produced by internal oxidation from the AgSn7,5 starting alloy (atomization of AgSn7,5, pressing, internal oxidation, sintering, extrusion), whereas AgNi10 was fabricated by classical powder metallurgy method (mixing of Ag and Ni, pressing, sintering, extrusion).

The mass losses after 50 000 switching cycles for materials are presented in Fig. 8. Dependence of contact mass loss on a number of switching cycles is shown in Fig. 9.

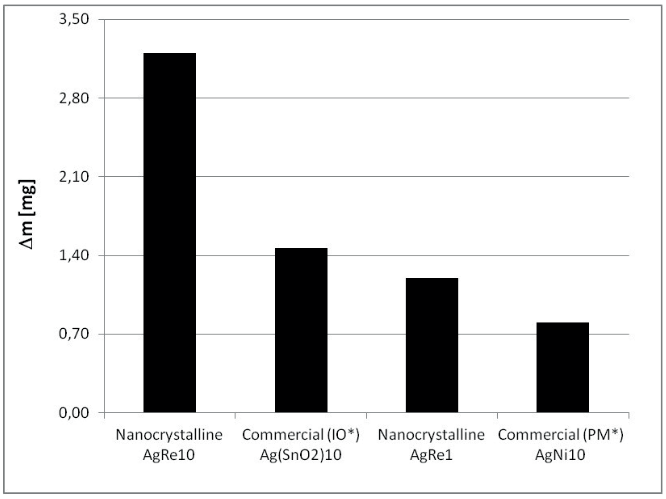

Fig. 8. A graphic representation of erosion-caused mass loss, measured for the contacts under test (average measurements values). DC current – 10A, voltage – 550V. (* IO – internal oxidation, PM – powder metallurgy)

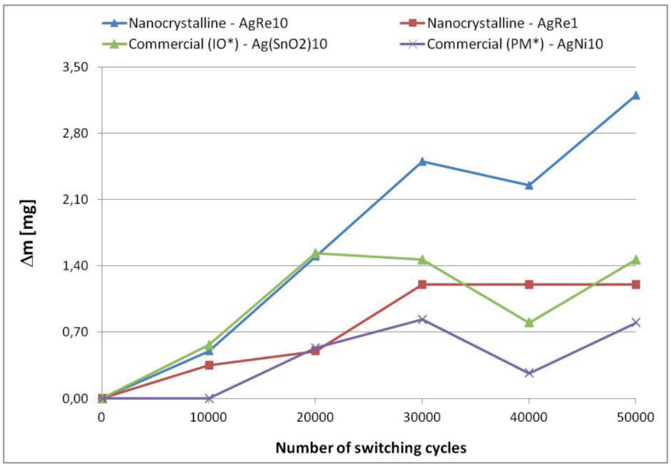

Fig. 9. Dependence of contact mass loss on a number of switching cycles. DC current – 10A, voltage – 550V. (* IO – internal oxidation, PM – powder metallurgy)

View of a surface of the AgRe1, AgRe10, Ag(SnO2)10 and AgNi10 contacts after arc erosion tests is shown in Fig 10.

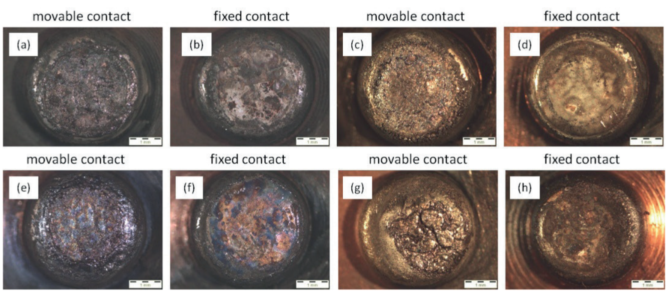

Fig. 10. Macro photographs of contact surface after the arc erosion testing. DC current – 10A, voltage – 550V: (a) and (b) nanocrystalline – AgRe10/Cu, (c) and (d) commercial (internal oxidation) – $Ag(SnO_2)10/Cu$, (e) and (f) nanocrystalline – AgRe1/Cu, (g) and (h) commercial (powder metallurgy) – AgNi10/Cu

The investigation of AC arc erosion was carried out in a testing system whose basic element is a testing device with a power drive [15]. It consists of several single current circuits with the tested contacts. Fig. 11. presents the structure of one such current circuit. Two identical tested contacts work in a horizontal axial system. The mobile contact remains in its normal position OFF as a result of the returnable spring action. The closing of contacts is obtained with the help of a cam mechanism with a double-arm lever and an electric engine. The possibility of manual adjustment of many mechanical parameters of the tested contacts is ensured. Current circuits of the testing device are connected to a resistant current circuit powered from a 230 V, 50 Hz network. The testing device is equipped with a computer system of measurement data (current, voltage) acquisition.

The testing system allows to test pairs of contacts (materials) quickly and simultaneously or a few different contacts each time. While testing contact life, contact resistance can be measured at 10 A current from an additional current source DC.

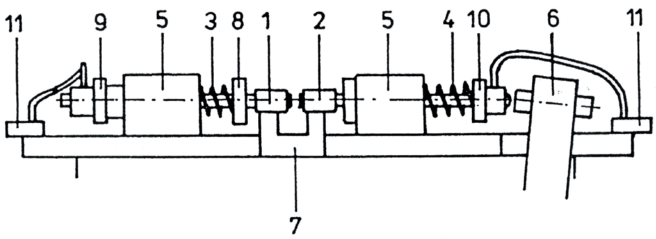

Fig. 11. Construction of a single current circuit of the testing device. 1 – fixed contact, 2 – mobile contact, 3 – contact spring, 4 – returnable spring, 5 – mobile contact guiding, 6 – live, 7 – current terminals

Mechanical and electrical test parameters were presented in Table 3. Fig. 13 shows characteristics of erosion of the composites under test and comparable commercial contacts. They are expressed by the contact mass losses in the function of a number of performed switching cycles. Fig. 12 presents the measurement results of average values of contact mass loss for this number of operations, for all tested contact specimens.

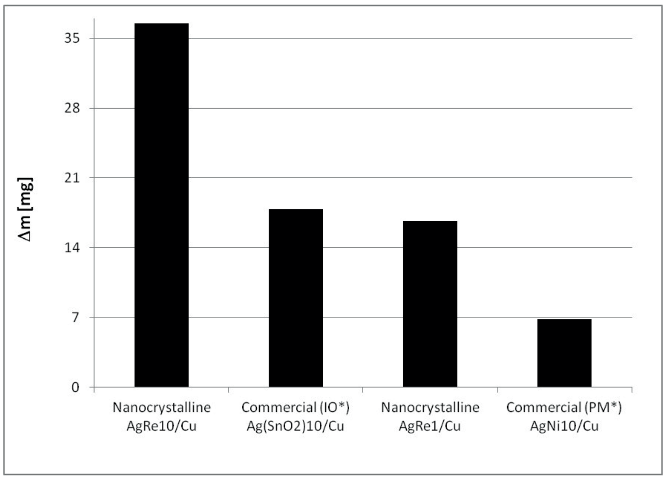

Fig. 12. A graphic representation of erosion measured for the contacts under test (average measurements values). AC current – 60A, voltage – 230V. (* IO – internal oxidation, PM – powder metallurgy)

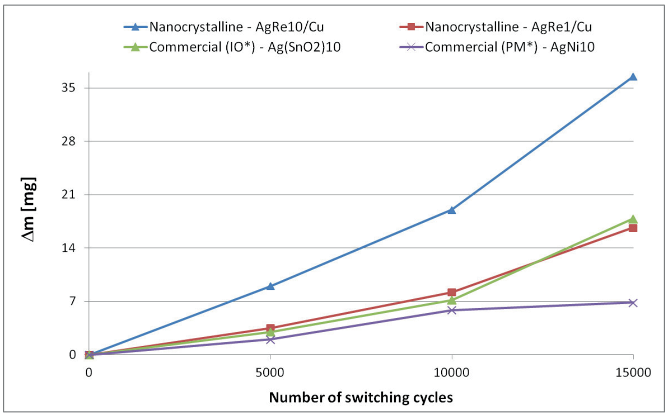

Fig. 13. Dependence of contact mass loss on a number of switching cycles. AC current – 60A, voltage – 230V. (* IO – internal oxidation, PM – powder metallurgy)

View of a surface e of the AgRe1, AgRe10, Ag(SnO2)10 and AgNi10 contacts after arc erosion tests is shown in Fig. 14.

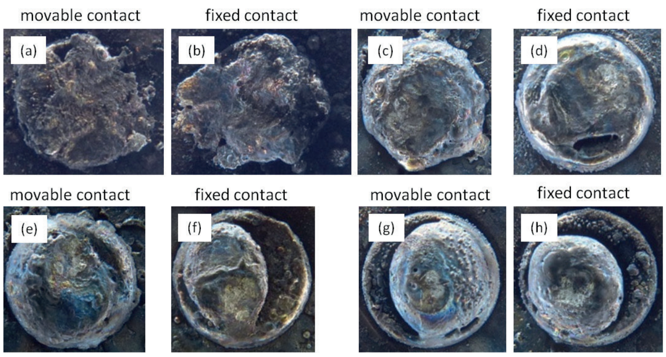

Fig. 14. Macro photographs of contact surface after the arc erosion testing AC current – 60A, voltage – 230V: (a) and (b) nanocrystalline – AgRe10/Cu, (c) and (d) commercial (internal oxidation) – Ag(SnO2)10/Cu, (e) and (f) nanocrystalline – AgRe1/Cu, (g) and (h) commercial (powder metallurgy) – AgNi10/Cu

3. Results and conclusions

The research works [7-10] resulted in the development of production technology of the AgRe contact rivets from traditional composites [7], and from nanocrystalline AgRe10 and AgRe1 composites [8-10]. The physical and mechanical properties of a 'classical' AgRe10 composite, and nanocrystalline AgRe10 and AgRe1 composite materials, have been summarized in Table IV. Measurements of these properties were made using the material samples taken from a wire having the diameter of 1.9 mm (AgRe10A and AgRe1C) and 2.5 mm (AgRe10B).

The AgRe10 nanocrystalline material, i.e. wire 2.5 mm in diameter, is characterized by relatively low plasticity expressed by the ratio $R_{0,2}/R_m$ = 0.99, therefore it cannot be subjected to cold drawing. For that reason, a softening annealing was applied, which resulted in clear plasticity increase. From the annealed wire, good quality bimetallic rivets were obtained. Their cross-section is shown in Fig.5. The semi-product, made from classical AgRe10 composite (wire, 4 mm in diameter) and subjected to cold drawing to the diameter of 1.9 mm with an overall reduction of about 77 %, exhibited suitable plastic properties to make its processing into solid and bimetallic rivets possible. Comparison of the mechanical properties of the nanocrystalline materials AgRe10 and AgRe1 clearly indicates that the AgRe1 composite exhibits higher plasticity, which enabled its drawing to the diameter of 1.9 mm without the use of softening annealing. Its limit of workability was relatively high, reaching $R_{0,2}/R_m$=0,87. The bimetallic rivets produced from this material were of a good quality. Its advantageous plastic properties indicate that it can be drawn to much lower diameters without the need of using softening annealing. The size of silver crystallites was at the following level: 60 nm in AgRe10, 57 nm in AgRe1. Microstructure of both composites (see Fig.4) reveals a uniform distribution of rhenium particles within a silver matrix, which contributes to good homogeneity of the physical and mechanical parameters over the whole length of fabricated wire. It should be emphasized that the process of plastic consolidation of the compacts be means of a hydraulic press operating under KOBO system plays a great role in reaching good contacts quality [14]. The arc erosion resistance of the contacts was tested at the 10 A direct current showing that the contact mass loss after 50 000 switching cycles was relatively low (see Fig. 8). In case of the contacts made from the AgRe1 composite, an average mass loss was very low (about 1.2 mg), whereas it was at the level of about 3.2 mg for the AgRe10 composite. Only slight degradation of the contact surface was observed both for the AgRe1 and AgRe10 contacts (see Fig 10). The tests were also performed using the 60 A alternating current showing much higher mass losses, reaching 13 mg and 36 mg for the AgRe1 and AgRe10 contacts, respectively. It should be noted that the 60 A alternating current used during the tests was relatively high for the 10BW4/1x2/2.5 contacts, and an excessive power density might cause heating of the contacts to excessively high temperature thus contributing to great mass losses.

TABLE 4

Physical and mechanical properties of selected composites

Material	R_m, MPa	$R_{0.2}$, MPa	$A_{11.3}$, %	Z, %	HV_1	Conductivity, MS/m	Size of Ag crystallites in the wire 1.9 mm in dia., nm
AgRe10A	243	224	7	14	70	52	-
AgRe10B	280	279	5	5	92	51	60
AgRe1C	308	267	8	70	82	55	57

A – classical composite material (1.90 mm in diameter)
B – physical and mechanical properties were examined using samples 2.5 mm in diameter directly after extrusion in a KOBO press
C – nanocrystalline composite (1.90 mm in diameter)

In conclusion, rhenium used in minor quantities might be a perspective material for application in contact materials as a substitute for the AgNi10 material used at present, which contains harmful (allergic) nickel, or commonly used $Ag(SnO_2)10$ composite. The technology for the production of wires and bimetallic contact rivets from a new nanocrystalline AgRe contact material containing up to 10 mass % Re has been developed. Moreover, physical, mechanical, technological and electrical parameters of the nano-composites with 1 and 10 % Re have been determined. It was found that there is potential possibility to use a new silver-based nanocrystalline material with up to 1 mass % of rhenium in the production of contact materials, which can be beneficial both from technological and economic points of view. This composite might be a substitute for the traditional $Ag(SnO_2)10$ contact material or other materials containing harmful (allergic) nickel, such as AgNi10.

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REFERENCES

[1] A. Krupkowski, Zasady termodynamiki i ich zastosowanie w metalurgii i metaloznawstwie, Kraków 1958.

[2] E. Walczuk, P. Borkowski et al., Report of Lodz University of Technology no.1869, Project no. R01 012 03, Unpublished.

[3] K. Wojtasik, M. Woch, Influence of rhenium addition on the structure and arc erosion resistance of tungsten-copper contact materials, 16th International Plansee Seminar 230-249 (2005).

[4] F. Hauner, D. Jeannot, J. Pinard, AgFe and $AgFe_2O_3$ Contact Materials for Voltage Switcher, 19-th Interrnational Conference on Electric Contact Phenomena, 317-323, Nurnberg (1998).

[5] L. Morin, N. Ben Jemaa, D. Jeannot, J. Pinard, L. Nedelec, J. P. Mercier, A study of new contacts materials under break arc in automobile area, 19-th International Conference on Electric Contact Phenomena, 89-96, Nurnberg (1998).

[6] A. Keil, Werkstoffe für Elektrische Kontakte: Springer Verlang, 1960.

[7] S. Księżarek, D. Kołacz, M. Woch, M. Czepelak, M. Osadnik, M. Karpiński, K. Marszowski, Ł. Wierzbicki, M. Kamińska, IMN Report 6886/2010, Unpublished.

[8] D. Kołacz, S. Księżarek, M. Czepelak, M. Kamińska, M. Staszewski, K. Bilewska, M. Karpiński, IMN Report 7002/11, Unpublished.

[9] M. Woch, S. Księżarek, D. Kołacz, W. Kurylak et al., Development of new nanocomposites using materials from mining industry, Grant agreement no: 263942-Nanomining.

[10] D. Kołacz, S. Księżarek, M. Czepelak, K. Rudnicki, M. Kamińska, M. Staszewski, K. Marszowski, Ł. Wierzbicki, M. Osadnik, IMN Report 7198/13, Unpublished.

[11] S. Księżarek, D. Kołacz, M. Czepelak, Z. Śmieszek, K. Marszowski, Technological aspects of plastic working of the Ag-Re(5, 8 and 10) wt % composite contact material, Hutnik – Wiadomości Hutnicze **8**, 633-636 (2011).

[12] S. Księżarek, M., Woch, T. Klir, D. Kołacz, M. Karpiński, K. Rudnicki, Environmentally friendly silver-based contact materials, Rudy i Metale Nieżelazne **57**, 8, 549-555 (2012).

[13] M. Woch, W. Missol, M. Lis, S. Księżarek, IMN studies into application of rhenium in non-ferrous metals processing, Rudy i Metale Nieżelazne **56**, 5, 266-271 (2011).

[14] W. Bochniak, Teoretyczne i praktyczne aspekty plastycznego kształtowania metali, Metoda KoBo, Wydawnictwo AGH, 2009.

[15] P. Borkowski, A. Augustyniak, A microprocessor control system for an automated stand for testing erosion of contacts designed for DC and AC contactors, IEICE Technical Report **109**, 287, 121-124, Tokyo 2009.