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Thermal stability of properties in silver – rare earth metals alloys

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Properties

ABSTRACT

Purpose: The objective of this work was to investigate the changes taking place in the structure and properties of Ag-La (0.5%) and Ag-mishmetal (1 and 4%) alloys caused by severe plastic deformation compared to the Ag+(7.5 wt %)Cu alloy and pure Ag materials.
Design/methodology/approach: Tests were made with the samples obtained casting and further plastic working included KOBO® extrusion process and drawing. Wires were annealed in temperature range 50-500ºC. The mechanical properties (at room temperature, elevated temperature and after annealing) and microstructure were examined (by the optical, scanning and transmission electron microscopy with EDS and electron diffraction analysis).
Findings: Structure of the extruded material was fine and homogenous. The alloys with an addition of lanthanum or mishmetal had high electrical conductivity, which was decreasing with an increase in the content of alloy additives. Fine coherent precipitates were found on the preferred planes in the silver matrix.
Practical implications: The alloy with an addition of La or mishmetal could be considered, after further investigations, as a material suitable for use in the production of electrical or electronic components operating at elevated temperatures or exposed to temperature changes.
Originality/value: This work has demonstrated that the properties of newly designed silver alloys with an addition of La or mishmetal exhibit temperature stability. It can be concluded from this study that an addition of rare earth metals to silver gives three main benefits: deoxidation during melting in an open furnace, very fine structure and precipitation hardening. The dispersion hardening with coarse particles (size about several μm) is very small. The wire made from this material could be easily produced by the developed processing methods, without the need to use annealing operations.
Keywords: Metallic alloys; Functional materials; Metallography; Electrical conductivity

1. Introduction

Silver is used in rapidly developing areas of modern science, including nanotechnologies and nanomaterials. Silver nanowires, 35 nm in average diameter, are produced by the combination of the porous anodic aluminium oxide template method with electrochemical deposition, which enables obtaining highly ordered nanostructured composites [1]. Due to their unique properties (chemical stability, catalytic activity and excellent electric conductivity), the finely dispersed silver nanoparticles have found various applications in many technologies, They are used as catalysts, transparent conductive coatings and as pigments for glasses and ceramics. Furthermore, nano-sized silver particles are also utilized as metal filler in both electrically conductive adhesives (ECAs) and inkjet conductive ink [2].

For a long time, silver has been used as a contact material in electric and electronic industries, and recently also in the production of contact tips or coatings. Most of these coatings are obtained by electroplating [3]. However, pure silver coating on the electric tips exhibits low mechanical properties. Therefore, new methods for increasing its mechanical properties without decreasing electrical conductivity of the tips are needed. In the work [4], the PVD ceramic coating (Ti/TiN, Nb/NbN, and CrN – hardness 2000-3500HV) was applied, whereas the second tip was made from pure silver, 70 HV in hardness. A combination of materials of a different hardness was obtained. Despite relatively high resistivity of the ceramic materials, the contact resistance was quite low, primarily due to the extensive contact area growth during fretting but also due to the fact that fretting enabled removal of the thin oxide or corrosion films from the ceramic coating surface. No welding between the coatings took place. The FEM model revealed that the maximum contact temperature is below 250^{o}C.

The presence of a thin pre-grown corrosion film on a top of the silver coating strongly influences the contact resistance, friction and degradation mechanism of the contact. Generally, the corrosion films reduce the tendency to adhesion between the contact surfaces, which subsequently reduces their deformation. This is particularly important in case of silver contacts operating in a sulphur atmospheres, where a film of silver sulphide (Ag_2S) is formed rapidly [5]. The refractory contacts materials with good functional properties can also be obtained by powder metallurgy methods [6]. However, electrical conductivity of these materials decreases to about 50% IACS. The wear of contact joint could be decreased by lubricants, but the contact resistance increases then with the increase of a number of contact cycles [7]. Improved properties exhibits the Ag-SnO_2 contact material [8] with an addition of Ti nanoparticles.

Important property of the contact materials is their ability to extinct electric arcs [9]. For the electric and electronic applications, silver films are also deposited onto the plastic substrates [10].

Different combinations of functional properties of the silver alloys can be obtained by the application of different options of metal working and heat treatment [11]. An addition of In to the Ag2%wt.Cu alloy makes that its strength increases, which results from the tendency of In atoms to segregate at grain boundaries, causing grain size refinement [12].

In this paper, silver alloys with an addition of lanthanum and with an addition of mishmetal were examined. These metals form intermetallic phases with silver. It can be expected [13] that the eutectic particles (silver – intermetallic phase) will form a dendritic structure after casting thus enabling dispersion hardening of these alloys. Due to the presence of hard intermetallic phase particles, which cause dislocation locking, this structure should improve mechanical properties of the material. The presence of the particles in grain boundaries slows down their migration and grain growth. Therefore, the fine-grained structure should be stable at elevated temperatures.

Dispersion hardening depends on the quantity, size and distribution of a hardening phase. At small amounts of the alloy additives, the decrease in electrical conductivity is insignificant.

There are many inconsistencies between the results from stoichiometric studies of the Ag-Ce system phases, especially in case of the Ag-rich compounds. The calculated maximum solubility of Ce in Ag is 0.04-0.9 at. % at 510^{o}C [14]. Solubility of La in Ag is about 0.6 at..% [15-16]. Therefore, precipitation of the intermetallic silver-rare earth metals phases is possible and it may result in alloy hardening and electrical conductivity decrease.

It can be seen in the diagrams of free energy of sulphides formation [17] that, in the cerium-containing silver alloy, CeS will be formed earlier than Ag_2S. The silver sulphide is responsible for tarnishing of a sliver surface. However, protective function of cerium is limited by its high affinity to oxygen.

2.Experimental procedure

Tests were made with Ag with 0.5 wt % La (AgLa0.5), Ag with 1wt % mishmetal (AgMm1), Ag with 4 wt % mishmetal (AgMm4) and Ag with 7.5 wt % Cu (AgCu7.5) alloys. The ingots were prepared by typical melting and alloying in an open-air induction furnace under the charcoal cover, and then cast into graphitoidal mould. The comparative material (besides sterling) was pure silver (Ag100) prepared by powder metallurgy methods. Because of the requirement that the obtained material should have a fine structure and dispersive distribution of hardening phases, samples in a shape of rollers, Φ 40 mm in diameter, were extruded by means of an oscillatory turning die press (KOBO). The samples were not heated before extrusion. The reduction degree after extrusion amounted to $\lambda = S_0/S_1 = 178$, which corresponded to the true strain of $\ln (S_0/S_1)=5.18$. Based on the results from earlier examination of the structure and properties of the materials extruded by the KOBO press it was decided to perform further processing by drawing, without any annealing operations. As a result, the wire Φ1,45 mm in diameter was obtained from Φ 40 mm ingot ($\lambda=S_0/S_F = 761$, $\ln (S_0/S_F)=6.64$) without any annealing process.

Microstructure of the obtained wire was examined using an optical microscope, scanning electron microscope and transmission electron microscope.

After drawing, the wires were subjected to tests on a tensile testing machine, carried out at elevated temperatures of 50, 100, 150, 200, 250 and 300^{o}C. The samples were kept in a given temperature for 30 minutes before the test.

Mechanical properties of the annealed samples were also examined. Samples were annealed at the temperatures of 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500^{o}C for 1 hour (pure silver up to 300^{o}C). After annealing, the samples were air-cooled and tested on a tensile test machine at a room temperature.

3. Results and discussion

The structure of the AgCu7.5 alloy after casting has been presented in Fig.1a. Many eutectic phase precipitates, several micrometers in size, have been observed. Some of the particles were undissolved copper. Copper was also dissolved (4-7%) in a silver matrix.

The AgLa0,5 alloy (Fig. 1b) had a dendritic structure after casting. A mixture of Ag, Ag_5La together with the oxides of these metals was found on the grain boundaries of pure silver. Free crystallization surface of the AgLa0.5 alloy has been presented in Fig. 2.

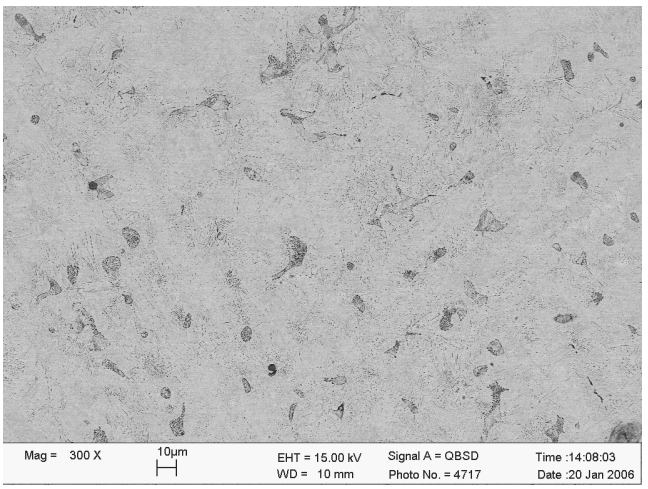
The structure of silver – mishmetal alloys after casting was similar to that of silver lanthanum alloy. Both alloys differed in the chemical compositions of grain boundaries, where a mixture

of Ag – Ag_4Ce, Ag_5La and the oxides was found. Volume fraction of these phases was higher in the alloy with higher mishmetal content. Further processing included extrusion performed by means of an oscillatory turning die press (KOBO). Macrostructure and microstructure on a cross-section of an extrusion butt was typical for the extrusion process (Fig. 3).

Significant changes in a microstructure obtained after extrusion (Figs. 4-5), compared to the dendritic structure after casting, were observed. The particles had a globular shape and their diameter over the cross-section was within a range of 2-5 µm. These particles were uniformly distributed within a matrix.

Volume fraction of these phases was increasing with the increase in the content of alloy additives. Size of the particles obtained after drawing ranged from 0.5 to 3 µm. The microstructure examination showed that the alloys had a fine structure (diameter of the matrix grains after extrusion was in a range of 2-3 µm, and for a pure silver in range of 10-20 µm).

a) AgCu7.5



b) AgLa0.5

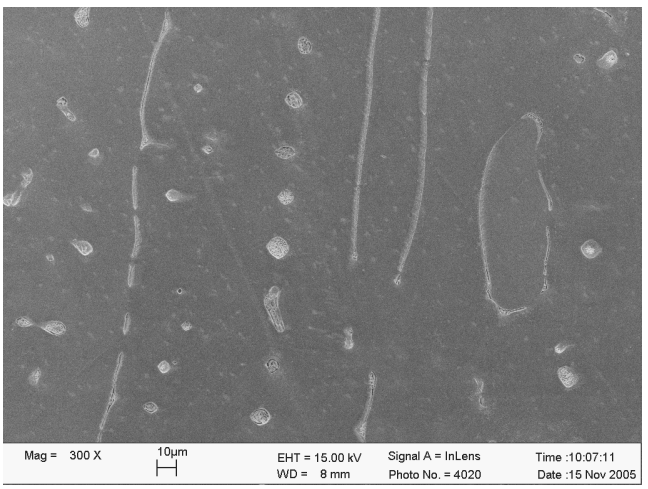
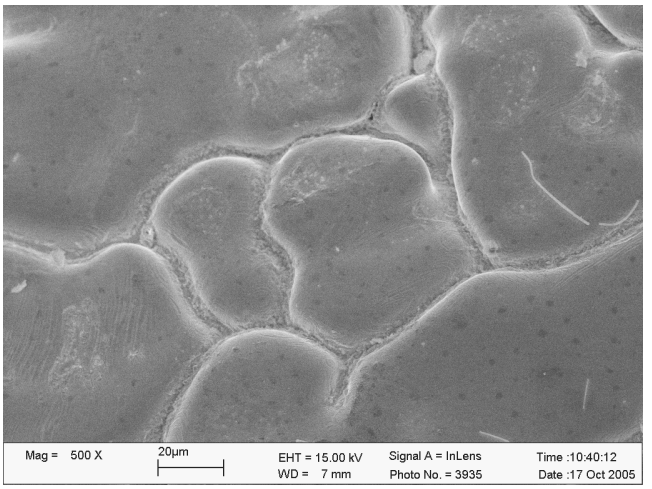
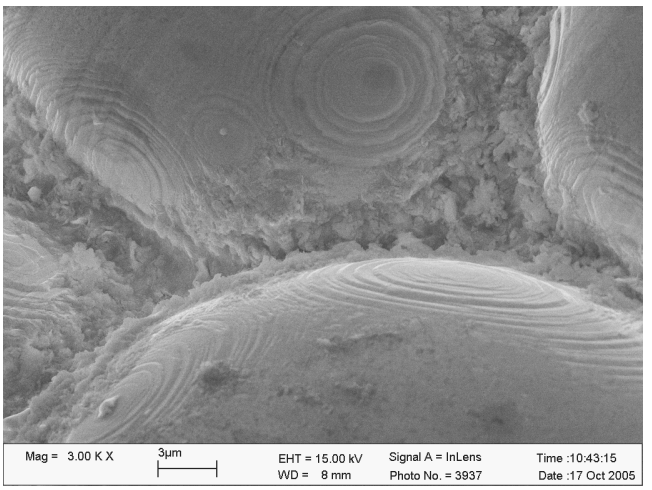


Fig. 1. Structure of the AgCu7.5 and AgLa0.5 alloys after casting



Mag. 500x



Mag. 3000x

Fig. 2. Free crystallization surface of the AgLa0.5 alloy

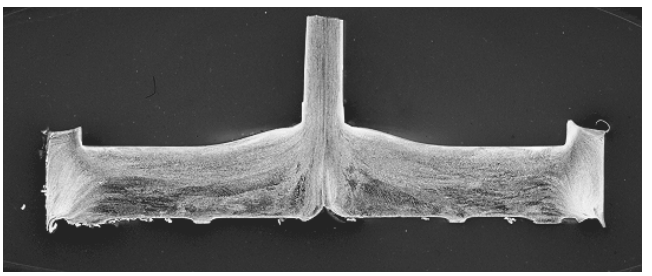


Fig. 3. Cross-section of an extrusion butt of the AgMm1 alloy

It should be emphasized that matrix grains on the cross-section and longitudinal-section were similar in shape and size. The particles on parallel micro-sections were forming bands coinciding with the extrusion and drawing directions. The plastic deformation by drawing resulted in further refinement of the structure.

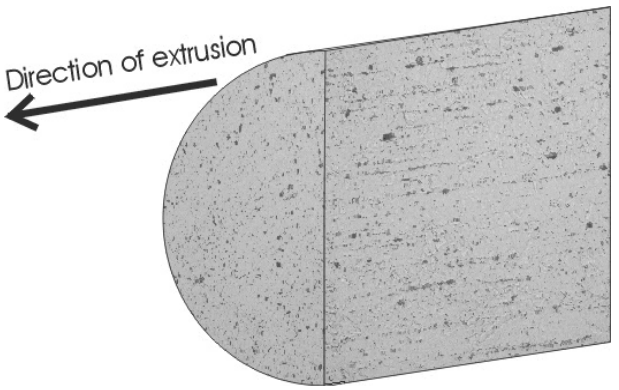


Fig. 4. Microstructure of the AgMM1 alloy after extrusion

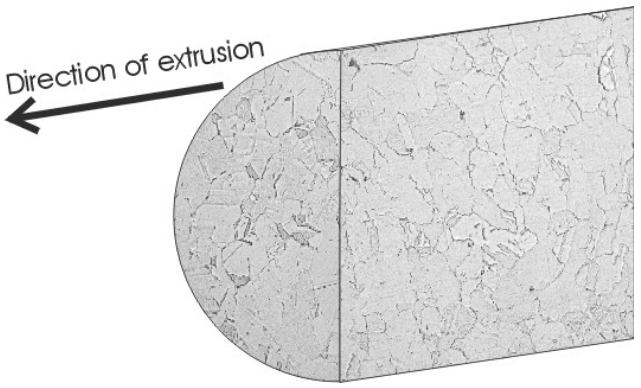


Fig. 5. Microstructure of pure silver after extrusion

After annealing, beginnings of recrystallisation process were observed, whereas the pure silver samples were already fully recrystallised.

Microstructure changes in the studied materials during their processing have been presented in Figs. 6-11.

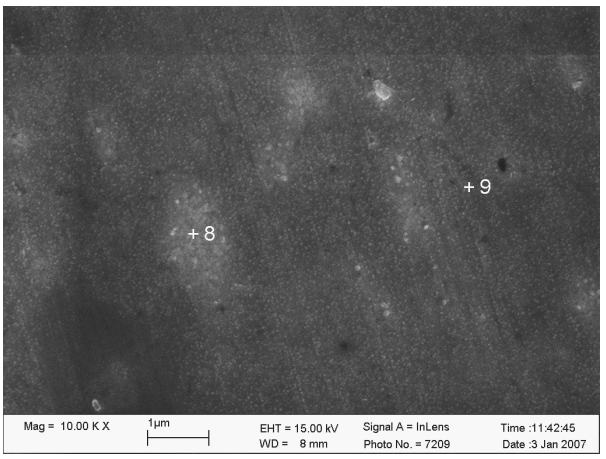


Fig. 6. Microstructure of the AgMM1 alloy after extrusion (λ=178), results of EDS analysis in micro-areas: 8: Ag=81.1%, La=6.3%, Ce=12.6%; 9: Ag=98,1, La=0.8%, Ce=1.1%

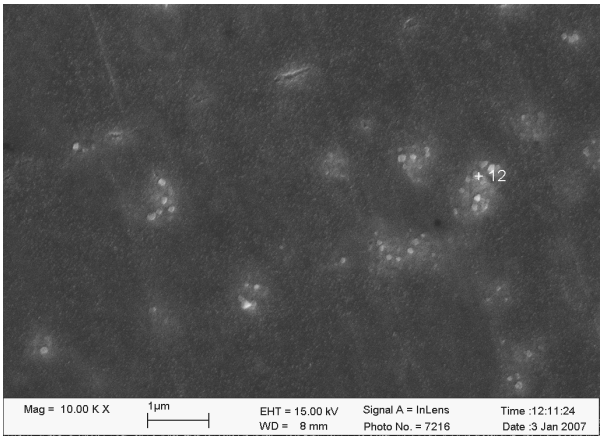


Fig. 7. Microstructure of the AgMM1 alloy after extrusion, drawing (λ=761) and annealing at 500°C for 1h; results of EDS analysis in micro-areas: 12: Ag=83.7%, La=5.2%, Ce=11.1%

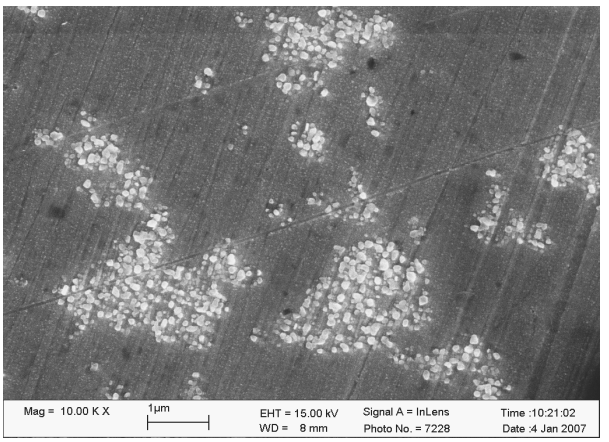


Fig. 8. Microstructure of the AgMM4 alloy after extrusion (λ=178)

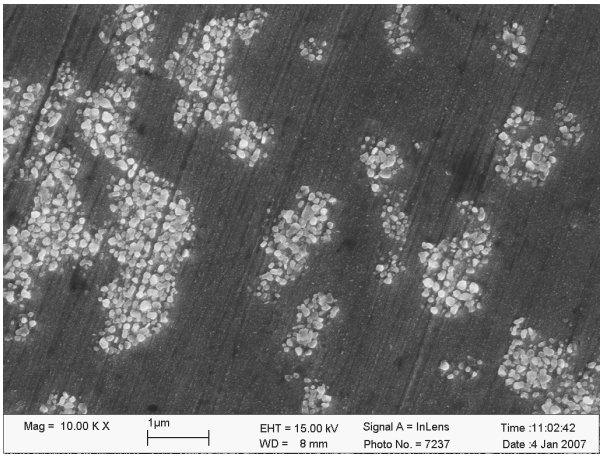


Fig. 9. Microstructure of the AgMM4 alloy after extrusion, drawing (λ=761) and annealing at 500°C for 1h

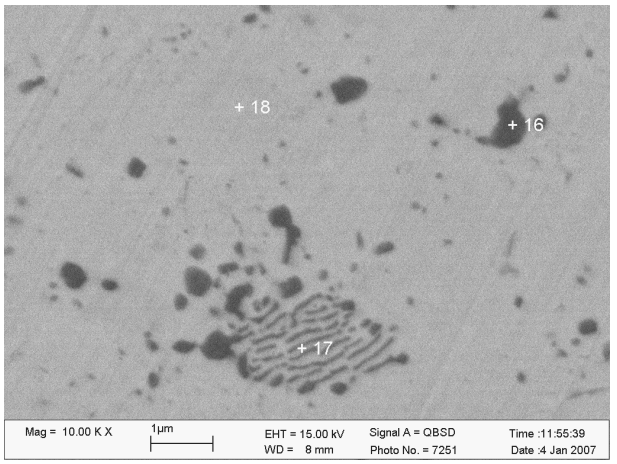


Fig. 10. Microstructure of the AgCu7.5 alloy after extrusion (λ=178); results of EDS analysis in micro-areas: 16: Ag=30.4%, Cu=69.6%; 17: Ag=61.5%, Cu=38.5%; 18: Ag=95.8%, Cu=4.2%

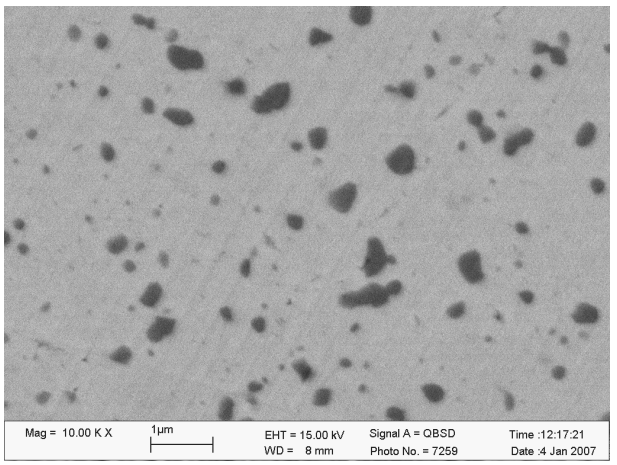
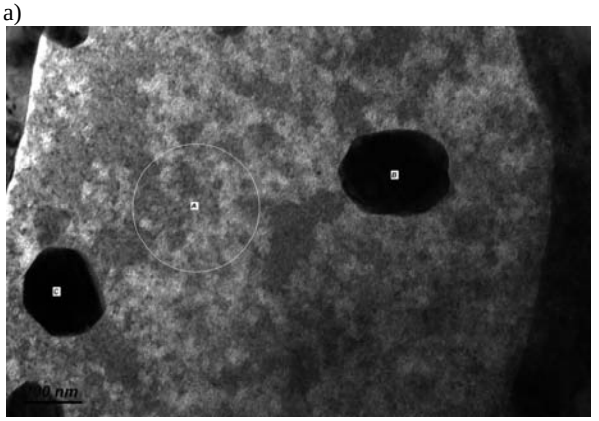


Fig. 11. Microstructure of the AgCu7.5 alloy after extrusion, drawing (λ=761) and annealing at 500°C for 1h

Electron transmission microscopy observations have revealed the presence of particles 200-400 nm in diameter, which probably favourably influence the mechanical properties and their stability. Particles in the alloys with an addition of lanthanum and mishmetal were examined using TEM equipped with EDS microanalyser. These particles are a mixture of silver, silver oxide and rare earth metals oxides (Fig. 12a). There were silver-enriched globular areas inside the particles (area B and C in Fig. 12a). The electron diffraction examination showed (Fig. 12b and c) that the particles did not contain metallic Ce or La. These particles were built from ultra-fine-grained, sub-nanometric oxides, with a grain size of about 1nm or below (according to the broadening of the smallest diffraction circle). However, the character of the electron diffraction patterns indicates that this structure was not amorphous (because there were more then three circles on a diffraction pattern).

a)



b)

c)

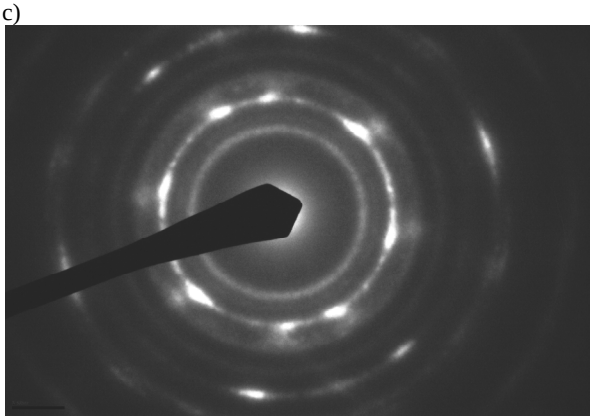


Fig. 12. Analysis of a particle of the AgMm1 alloy, TEM, mag. 25000x: a) structure inside the particle with marked points of EDS analysis (weight %):

area	O	Ag	La	Ce
A	6.91	68.82	6.42	15.24
B	2.12	90.97	1.86	4.39
C	-	99.04	0.54	0.71

b) area, where electron diffraction analysis has been carried out (view through the smallest selective diffraction aperture, diameter of about. 140 nm); c) electron diffraction analysis carried out in a marked area

TEM investigation of a silver matrix have revealed (Fig. 13) the presence of second phase precipitates on the preferred planes. However, the EDS analysis has not revealed any other elements except for silver. It can be concluded, therefore, that these were precipitates of intermetallic phases Ag_5La, Ag_4Ce, which can stabilize the microstructure and also increase and stabilize mechanical properties of the alloys with an addition of lanthanum or mishmetal.

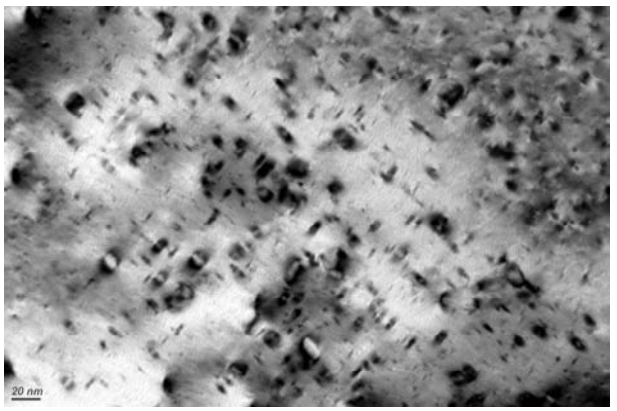


Fig. 13. Microstructure of a silver matrix of the AgMm1 alloy, magn. 60000x

Mechanical properties of the AgLa0.5 alloy after drawing was similar to those of a deformed pure silver (λ=178). The strengthening of the AgMm1 and AgMm4 alloys was higher at higher content of mishmetal as an additive. For the highest mishmetal content (AgMm4), the strengthening was close to that for comparative AgCu7.5 alloy, which had the highest mechanical properties after drawing.

Mechanical properties of the cold-worked pure silver decreased considerably at the annealing temperature of 150°C and above (Fig. 14). These properties for the silver-lanthanum and silver-mishmetal alloys, however, remained stable up to 300 - 350°C. The highest mechanical properties had the Ag+7.5Cu alloy, but at the annealing temperature of 200°C and above they started to decrease dramatically. The curves illustrating the changes in properties during tensile tests performed at elevated temperature (Fig. 15) seem to be shifted towards lower temperatures in comparison with the curves in Fig. 14. However, the curves for pure silver look very similarly in both cases. The yield points of the silver-lanthanum, silver-mishmetal and Ag+7.5Cu alloys, measured during tensile test at the temperature of 250°C and above, had a similar value of about 200 MPa.

The wire from AgCu7.5 alloy had strongly tarnished surface after extrusion, whereas the surface of a wire from the AgMm4 alloy was slightly tarnished. The rest of the examined wires had bright and glossy surface. After drawing, all wires had bright and glossy surface, and annealing at the temperature of 200°C and above for 1 hour caused tarnishing of the AgCu7.5 alloy only.

The highest electrical conductivity after drawing was obtained for pure silver (60.9 MS/m). Conductivity of the silver-lanthanum alloy was close to that of pure silver. Conductivity of the silver-mishmetal alloys was decreasing with the increase of the content of this alloy additive (Fig. 16).

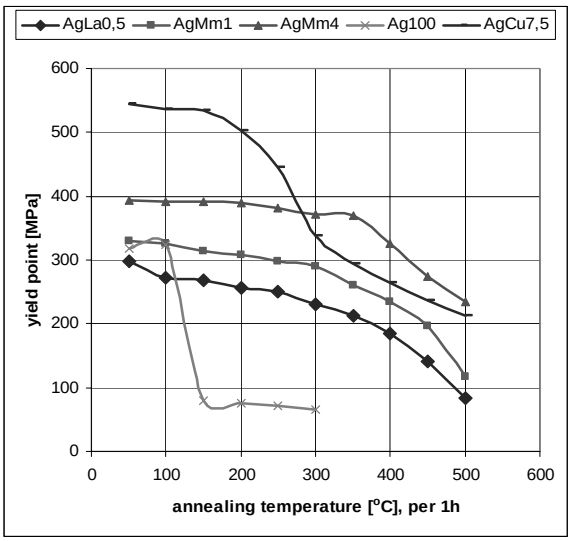


Fig. 14. Tensile strength versus annealing temperature

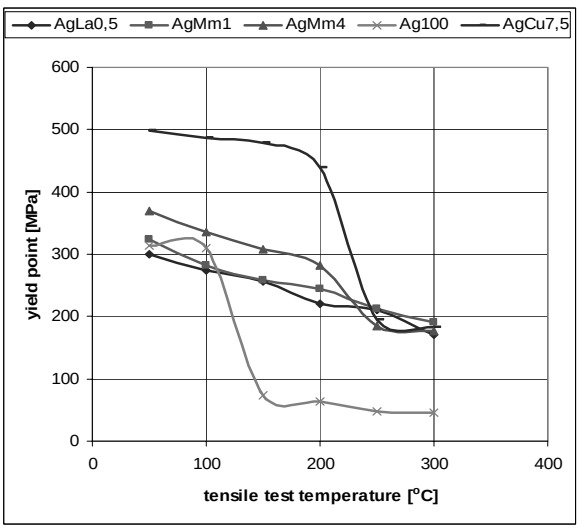


Fig. 15. Yield point versus tensile test temperature

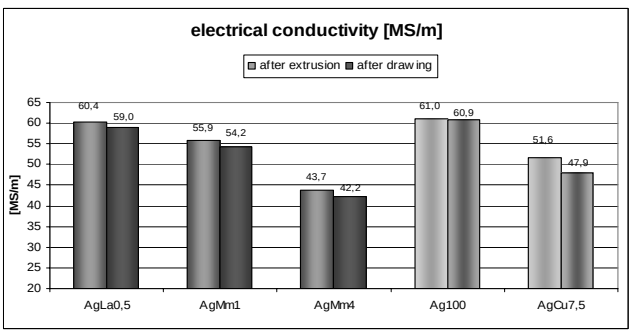


Fig.16. Electrical conductivity of the examined wires after extrusion and drawing

4. Conclusions

The microstructure obtained after KOBO® extrusion process was fine and uniform. Besides, the size and shape of the grains were similar on a cross-section and longitudinal section. Processing of the material by drawing resulted in further refinement of the structure. Particles on the longitudinal sections formed the bands coinciding with the extrusion and drawing directions.

Electrical conductivity of the investigated alloys was decreasing with the increase of a content of alloy additives. Plastic deformation caused by drawing also resulted in a decrease in electrical conductivity: from 60.4 MS/m to 59 MS/m in the Ag0.5La alloy, from 55.9 MS/m to 54.2 MS/m in the AgMM1 alloy and from 43.7 MS/m to 42.2 MS/m in the AgMM4 alloy. An increase in mechanical properties of the reference AgCu7.5 alloy subjected to drawing resulted in a decrease of its electrical conductivity to about 50 MS/m. In case of pure silver this decrease was small: from 61 MS/m to 60.9 MS/m.

The electron transmission microscopy observations have revealed the presence of the oxide particles (200-5000 nm in diameter) in silver – lanthanum and silver – mishmetal alloys. These particles had ultra-fine-grained, sub-nanometric structure. Fine coherent precipitates were found on the preferred planes in the silver matrix of the silver-lanthanum or silver-mishmetal alloys. These precipitates contributed to the increase of mechanical properties and their stabilization at elevated temperatures. However, the EDS analysis in a matrix area has not revealed the presence of any rare earth metals or oxygen. It is possible that these precipitates were intermetallic phases Ag_4Ce, Ag_5La. The absence of oxygen in a silver matrix indicates that the oxide particles in these alloys are the products of liquid silver de-oxidation by lanthanum, cerium and other rare earth metals, taking place during melting in an open furnace.

Summarising, it can be concluded from this study that an addition of rare earth metals to silver gives three main benefits:

- deoxidation during melting in an open furnace,
- very fine structure is obtained due to the presence of many particles as crystallisation nuclei, and
- precipitation hardening.

The dispersion hardening with coarse particles (size about several μm) is very small.

Results from this investigation confirmed that the proposed silver alloys with an addition of lanthanum or mishmetal exhibit increased stability of the mechanical properties at elevated temperatures. They can be considered, therefore, as the materials suitable for application in the production of electrical or electronic components operating at elevated temperatures or exposed to rapid temperature changes.

The alloy with an addition of 4% of mishmetal could be used in producing parts which can be exposed to greater temperatures (above 300°C). Although this alloy has lower electrical conductivity than that of the AgCu7.5 alloy, it exhibits better mechanical properties at the temperatures above 300°C.

It is worth mentioning that mechanical properties of these alloys at the temperature of above 200°C were close to those of the Ag+7.5Cu alloy which had much better mechanical properties at a room temperature.

The investigated materials were fabricated in an open furnace under the conditions close to the industrial ones. It is planned to investigate these materials using vacuum furnace to fabricate them, with special emphasis put on the possibility of their precipitation hardening and on its influence on the mechanical properties and electrical conductivity.

Acknowledgements

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References

[1] R. Yang, Ch. Sui, J. Gong, L. Qu, Silver nanowires prepared by modified AAO template method, Materials Letters 61 (2007) 900-903.
[2] H.W. Lin, W.H. Hwu, M.D. Ger, The dispersion of silver nanoparticles with physical dispersal procedures, Journal of Materials Processing Technology (2008), in print.
[3] D.Vanek, Selective electrofinishing, SIFCO Selective Plating, Cleveland.
[4] A. Rudolphi, S. Jacobson, On the use of ceramic PVD coating to replace metallic coatings in electrical contacts, Surface and coating technology 89 (1997) 270-278.
[5] A. Rudolphi, S. Jacobson, Stationary loading, fretting and sliding of silver coated copper contacts – influence of corrosion films and corrosive atmosphere, Tribology International 30/3 (1997)165-175.
[6] F. Findik, H. Uzun: Microstructure, hardness and electrical properties of silver-based refractory contact material, Materials and Design 24 (2003) 489-492.
[7] N. Myshkin, V. Kontchits, Y. Kirpichenko, L. Markova, Wear of contact elements in electromechanical switches, Wear 181-183 (1995) 691-699.
[8] X.M. Liu, S.L. Wu, Paul K. Chu, C.Y. Chung, J. Zheng, S.L. Li, Effects of coating process on the characteristics of Ag–SnO_2 contact materials, Materials Chemistry and Physics 98 (2006) 477-480.
[9] E. Vinaricky, U. Harmsen, Effect of silver/metal oxide contact materials on the extinction of short ac arcs, Metall 25/7 (1971) 749-754.
[10] N. Sankir, R. Claus, An alternative method for selective metal deposition onto flexible materials, Journal of Materials Processing Technology 196 (2008) 155-159
[11] H.J. Shin, H.T. Jeong, D.N. Lee, Deformation and annealing textures of silver wire, Materials Science and Engineering A279 (2000) 244-253.
[12] R.H. Nada, Precipitation kinetics in Ag–2wt% Cu and Ag–2wt% Cu–0.5wt% In alloys during transformation, Physica B 349 (2004) 166-173.
[13] Z Kędzierski, Phase transition in condensed systems, Didactic-Scientific Press, Kraków 2003 (in Polish).

[14] F. Yin, M. Huang, X. Su, P. Zhang, Z. Li, Y. Shi, Thermodynamic assessment of the Ag–Ce (silver–cerium) system, Journal of Alloys and Compounds 334 (2002) 154-158.
[15] Z. Li, X. Su, F. Yin, Ch. Chen, On the thermodynamic assessment of the Ag–La system, Journal of Alloys and Compounds 299 (2000) 195-198.
[16] S.V. Meschel, O.J. Kleppa, Thermochemistry of some binary alloys of silver with the lanthanide metals by high temperature direct synthesis calorimetry, Journal of Alloys and Compounds 376 (2004) 73-78.
[17] S. Mrowec, Outline of metal oxidation theory) Silesian Press 1971 (in Polish).