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Stabilization of mechanical properties in silver alloys by addition of lanthanides

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Materials

ABSTRACT

Purpose: Silver alloys intended for industrial application should characterise by high electrical conductivity (as pure silver) as well as high mechanical and functional properties, stable also at elevated temperature. The objective of this work was to investigate the mechanical properties stability 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 by casting and further plastic working included KOBO® extrusion process and drawing. Wires were annealed in temperature range 50 - 500°C. The mechanical properties (at room temperature, elevated temperature and after annealing) and microstructure were examined. The values of yield strength obtained in a tension tests have been compared to the values calculated theoretically.
Findings: Additive of rare earth metals contributed to fine structure obtaining, particles formed in grain boundaries stabilized microstructure at elevated temperature. Increase of mechanical properties of investigated alloys was connected with presence of fine precipitations in silver matrix, which confirmed susceptibility to precipitation hardening of silver – mishmetal alloys.
Research limitations/implications: Ability of new alloys to precipitation hardening should be confirmed by further investigations, including solution heat treatment and ageing, also for materials prepared in vacuum furnace.
Practical implications: Stability of mechanical properties at elevated temperature, gives possibility to use of new silver allays for producing elements designed to operate at elevated temperatures or exposed to rapid temperature changes. Increased mechanical properties and good tarnish resistance indicates possibility of new applications of investigated alloys in jewellery and medicine, after additional and essential investigations.
Originality/value: 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 and silver alloys are most often associated with beautiful tableware, jewellery and coins. Although, we have to consider that more then half or world silver demands are from growing industrial requirements. It is difficult to imagine development in electronic and electrotechnics without silver and silver alloys. Silver alloys intended for industrial application should characterise by high electrical conductivity (as pure silver) as well as high mechanical and functional properties, stable also at elevated temperature. Silver alloys designed for producing an electrical contacts should also have high corrosion and erosion resistance, high temperature resistance, ability to extinct of electric arcs and it can not weld during work. Alloy additives are

used to meet these requirements, particularly such which cause precipitation hardening or dispersion hardening [1-3]. These mechanisms are well known in platinum alloys [4-6] and copper alloys [7-9]. It is important that electrical conductivity decreasing have to be small. That's why amount of alloy additive is limited. Chosen alloy additives should slow down dislocation movement and grain boundaries migration, causing improvement in mechanical properties. The presence of particles in grain boundaries slows down grain growth at elevated temperature, which contribute to stabilization of properties. Increase of mechanical properties depend on particle size and dispersity. Another useful feature should be fine structure, providing good functional properties [10-12].

2. Material ve method

Investigation material was alloys obtained classically by melting in induction furnace (in graphitoidal crucible). As a charge pure silver, electrolytic copper and mishmetal (mixture of rare earth elements containing: Ce -52.4%, La – 21.1%, Nd – 13.3%, Pr – 8.2%) have been used. Liquid metal was cast into graphitoidal mould. The ingots (ϕ 40 x 55 mm) were prepared with materials:

- Silver alloy with addition of 1%wt. mishmetal marked: AgMM1;
- Silver alloy with addition of 4%wt. mishmetal marked: AgMM4;
- Silver alloy with addition of 7.5%wt. copper marked: AgCu7.5.

The another comparative material was pure silver (Ag100) prepared by powder metallurgy methods (ϕ 40 x 55 mm compact). Ingots, Φ 40 mm in diameter, were extruded by means of an oscillatory turning die press (KOBO® method) in one pass obtaining 3 mm diameter wire. The reduction degree after extrusion amounted to $\lambda = S_0/S_1 = 178$, which corresponded to the true strain of $\ln (S_0/S_1)=5.18$. Further plastic working have been provided by drawing from diameter 3 mm to diameter 1.45 mm. In this process 1.45 diametr wire have been obtained from 40 mm diameter ingot ($S_0/S_K = 761$, $\ln(S_0/S_K)=6.64$) without any annealing operations.

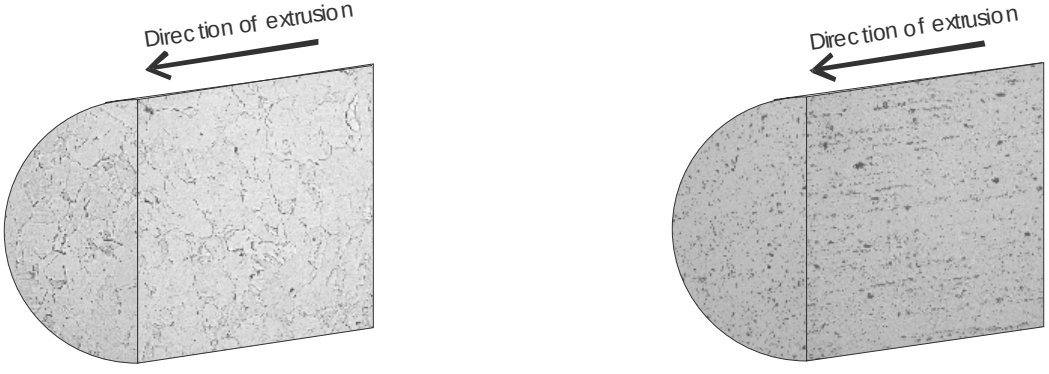
Microstructure of the obtained wire was examined using an OLYMPUS optical microscope, ZEISS LEO GEMINI 1525 scanning electron microscope equipped with EDS and JEOL JEM-2010 transmission electron microscope equipped with EDS. Mechanical properties of wires on every processing stage, in room temperature using INSTRON tensile test machine have been provided.

The 1.45 diameter wires were subjected to tests on a tensile testing machine at elevated temperatures of 50, 100, 150, 200, 250 and 300°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°C for 1 hour (pure silver up to 300°C). After annealing, the samples were air-cooled and tested on a tensile test machine at a room temperature.

Changes in electrical conductivity have been investigated using Foerster sigmatest and Thomson bridge.

3. Results and discussion

Detailed description of microstructure investigations after, compacting and sintering, casting, as well as after KOBO® extrusion have been published in former works [13-15]. Basing on microstructure investigations results we can found that after extrusion process matrix grains on the cross-section and longitudinal-section were similar in shape and size. Diameter of the matrix grains after extrusion was in a range of 2-4 μm, and for a pure silver in range of 17-20 μm. The particles on parallel micro-sections were forming bands coinciding with the extrusion direction. The particles had a globular shape over the cross-section and their diameter was within a range of 1-3 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. An example of microstructure after extrusion with KOBO® method have been resented on Fig. 1. Investigation of a silver matrix have been provided using transmission electron microscopy TEM. Matrix microstructure of AgMM1 alloy have been presented on Fig. 2. These investigations revealed the presence of second phase precipitates on the preferred planes (size several nanometres). 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 or pure metals, which stabilize the microstructure and also increase and stabilize mechanical properties of the alloys with an addition of mishmetal.



Ag100 AgMM1

Fig. 1. Microstructure of Ag 100 and Ag MM1 after KOBO® extrusion

The plastic deformation by drawing resulted in further refinement of the structure, up to particle size in range 1-2 μm. After annealing in fixed conditions (time-temperature), there were beginnings of recrystallization process [15].

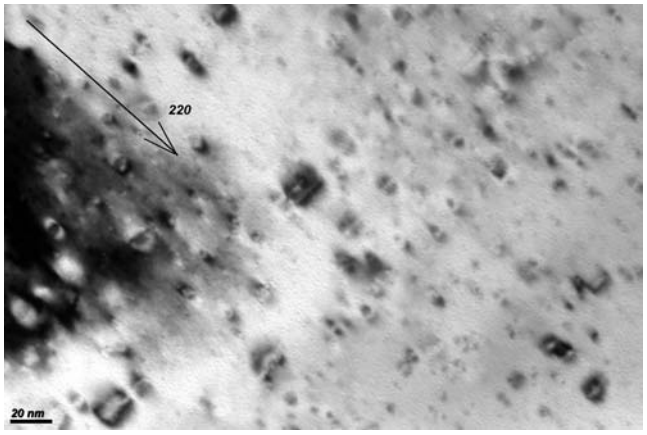


Fig. 2. Matrix microstructure of AgMM1 alloy, TEM

The strengthening of the AgMm1 and AgMm4 alloys after drawing was higher at higher content of mishmetal as an additive (Fig. 3). For the highest mishmetal content (AgMm4), the strengthening was close to that for comparative AgCu7.5 alloy.

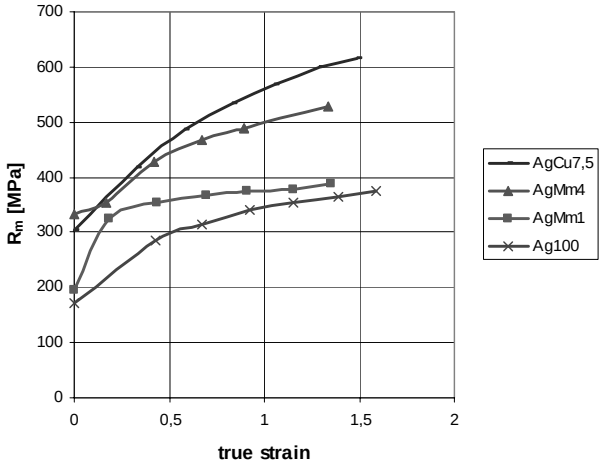


Fig. 3. Tensile strength R_m versus true plastic strain during drawing

Yield strength of silver-mishmetal alloys decreased gently with increasing of tensile test temperature, for pure silver value of yield strength decreased considerable already at tensile test temperature 100°C. AgCu7.5 alloy demonstrate significant decrease of yield strength at tensile test temperature 200°C. The yield strengths of the AgMM1, AgMM4 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 (Fig. 4).

Changes of yield strength of investigated materials cold drawn to the diameter 1.45 mm and then annealed in fixed temperature by 60 minutes (after cooling tensile tested in room temperature) have been presented on Fig. 5. 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. These properties for the silver-mishmetal alloys, however, remained stable up to 300 - 350°C, increasing with increase of amount of alloy additive. Mechanical properties of the cold-worked pure silver decreased considerably at the annealing temperature of 150°C and above.

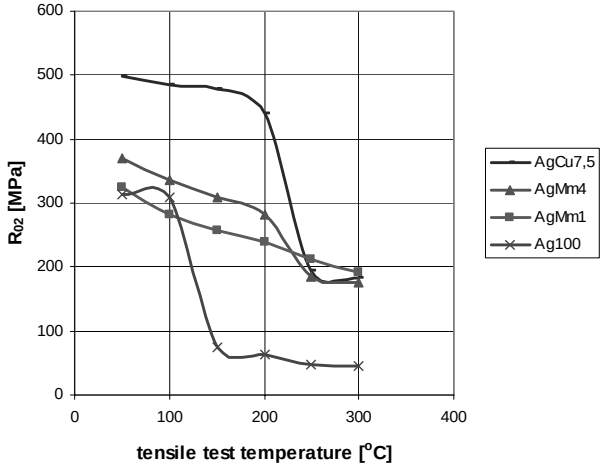


Fig. 4. Yield strength R_{02} versus tensile test temperature

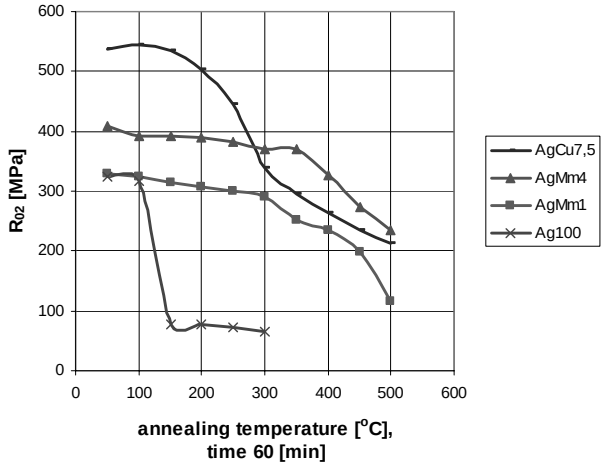


Fig. 5. Yield strength R_{02} versus annealing temperature (annealing time 60 min)

3.1. Theoretical calculation of yield strength value

Theoretical calculation of yield strength value for investigated material ware carried out for developing of properties and technological process [16-18].

$$\sigma_{0.2} = \sigma_0 + \sigma_{HP} + \sigma_{OR} \quad (1)$$

where:

σ_0 – Peierls stress neglible in fcc material,
σ_{HP} – stress caused by grained structure according to the Hall-Petch's formula,
σ_{OR} – stress caused by presence of hard particles in the matrix according to the Orowan's formula.

$$\sigma_{HP} = k_{HP} d^{-1/2} \tag{2}$$

where:
k_{HP} –Hall-Petch'a equitation coefficient assumed 4.5 MPa mm $^{1/2}$,
d – matrix grain diameter.

$$\sigma_{OR} = 0.9M \frac{[\ln(8r_s/b)]^{3/2}}{[\ln(L/b)]^{1/2}} \left[\frac{K^{edge}}{b(L-2r_s)} \right] \tag{3}$$

$$r_s = \frac{\pi}{4} r_{cz}, \quad K^{edge} = \frac{Gb^2}{4\pi(1-\nu)}, \quad L = \sqrt{\frac{32}{3\pi f}} r_s \tag{4}$$

where:
M –Taylora factor, assumed 2.45,
b –Burgers vector, assumed 0.288 nm,
K^{edge} – pre-logarithmic line tension factor,
L – mean planar dispersoid spacing,
r_{cz} – mean radius of the particles,
G – shear modulus, assumed 29000 MPa,
ν –Poisson's ratio assumed 0.38,
f – volume fraction of dispersoids (for calculations planar fraction according to the Cavalieri-Hacquert's formula have been assumed).

Metallographic data obtained during microstructure analysis have been used for the calculations. Results have been presented in Tables 1 and 2.

As we can se the calculated values were lower then obtained during tension test. Analyzing these differences we have to consider that metallographic data, used for calculations, were from optical electron scanning microscopy investigations. Because lock of possibility to proper identification of grains and particles, calculations were provided for object bigger than 500 nm. Transmission electron microscopy revealed presence of smaller particles and coherent precipitates with diameter about 20 nm, which was not taken into consideration.

Planar fraction of particles have been decreased after drawing (comparing to the extruded material) because of structure refinement and lack of possibility to measure of particles smaller then 500 nm with selected method.

Content of Ce and La in particles, visible with electron scanning microscope, measured with energy dispersive detector (EDS), have been changed in wide range 2-30 wt.%. These changes were due to complex particle structure and local fraction differences of rare earth metals oxides, silver oxides and metallic silver. EDS analysis area taken from a small particles could also contain matrix area close to the particles. To simplify, we assumed that mean content of rare earth metals in particles was 15 wt.%. Multiplying this value by planar fraction of particles we obtained amount of alloy additive occurring in the particles.

Table 1.
Calculations results for alloys after extrusion

Alloy	Mean diameter of matrix grain [mm]	Mean diameter of particles [nm]	Planar fraction of particles	σ_{HP} [MPa]	σ_{OR} [MPa]	$\sigma_{HP}+\sigma_{OR}$ [MPa]	σ_{02} from tensile test [MPa]
AgMM1	0.00315	1110	0.0634	80.18	5.98	86.15	90.3
AgMM4	0.00232	1470	0.2134	93.43	12.84	106.26	152

Table 2.
Calculations results for alloys after extrusion, drawing and annealing 500°C/h

Alloy	Mean diameter of matrix grain [mm]	Mean diameter of particles [nm]	Planar fraction of particles	σ_{HP} [MPa]	σ_{OR} [MPa]	$\sigma_{HP}+\sigma_{OR}$ [MPa]	σ_{02} from tensile test [MPa]
AgMM1	0.00196	920	0.0427	101.65	5.37	107.02	116
AgMM4	0.00156	1340	0.1765	113.93	11.57	125.50	234

Table 3.
Calculations results of alloy additive amount of investigated materials, divided on particles and matrix, after extrusion

Alloy	Avarage content of rare earth metals in particles [%wt]	Planar fraction of particles [%]	Amount of alloy additive occurred in particles [%wt]	Total amount of alloy additive [%wt]	Missing difference = content of rare earth metals in matrix [%wt]
AgMM1	15	6.34	0.95	1	0.05
AgMM4	15	21.34	3.2	4	0.8

Table 4.
Calculations results of alloy additive amount of investigated materials, divided on particles and matrix, after extrusion, drawing and annealing 500°C/h

Alloy	Avarage content of rare earth metals in particles [%wt]	Planar fraction of particles [%]	Amount of alloy additive occurred in particles [%wt]	Total amount of alloy additive [%wt]	Missing difference = content of rare earth metals in matrix [%wt]
AgMm1	15	4.27	0.64	1	0.36
AgMm4	15	17.65	2.65	4	1.35

This values were lower than amount of mishmetal added into the alloy and analyzed in further processes (Tables 3 and 4). So, we could expect that some amount of rare earth metals occurs in a matrix.

Assuming after simplification, that missing difference was planar fraction of coherent participations in a metal matrix, new term σ_{OR}' of Equitation (1) was added corresponding to the hardening by precipitations 20 nm in size.

Thus equitation took form:

$$\sigma_{0.2} = \sigma_0 + \sigma_{HP} + \sigma_{OR} + \sigma_{OR}' \quad (5)$$

Calculations results, presented in Tables 5 and 6, were close to the values obtained in tension tests.

Table 5.
Comparison of yield strength calculated theoretically and obtained in tension test of investigated alloys, after extrusion

Alloy	σ_{02} from Equitation (5) [MPa]	σ_{02} from tension test [MPa]
AgMm1	97	90.3
AgMm4	156	152

Table 6.
Comparison of yield strength calculated theoretically and obtained in tension test of investigated alloys, after extrusion, drawing and annealing 500°C 1h

Alloy	σ_{02} from Equitation (5) [MPa]	σ_{02} from tension test [MPa]
AgMm1	138	116
AgMm4	194	234

Electrical conductivity measurement results have been presented on Fig. 7. Electrical conductivity silver –mishmetal alloys decreased significantly after casting. Structure reconstruction during extrusion in KOBO® process caused increasing of electrical conductivity.

Obviously, highest electrical conductivity after extrusion had a pure silver - about 61 MS/m, classical alloy AgCu7.5 had electrical conductivity about 50 MS/m. In silver mishmetal alloys electrical conductivity was in range 43-55 MS/m, decreasing with increasing of alloy additive content. Cold drawing slightly decreases electrical conductivity of all investigated materials.

4. Conclusions

Basing on carried out an investigations we can conclude the metal processing with KOBO® method caused significant changes in primal casting-dendrytic structure. The new structure was banding with recrystalized matrix. Changes in microstructure were connected with improving of mechanical and electrical properties of investigated materials.

Additive of rare earth metals contributed to fine structure obtaining, particles formed in grain boundaries stabilized microstructure at elevated temperature.

Increase of mechanical properties of investigated alloys was connected with presence of fine precipitations in silver matrix, which confirmed susceptibility to precipitation hardening of silver –mishmetal alloys.

Ability of new alloys to precipitation hardening should be confirmed by further investigations, including solution heat treatment and ageing, also for materials prepared in vacuum furnace.

Stability of mechanical properties at elevated temperature, gives possibility to use of new silver allays for producing elements designed to operate at elevated temperatures or exposed to rapid temperature changes.

Increased mechanical properties and good tarnish resistance indicates possibility of new applications of investigated alloys in jewellery and medicine, after additional and essential investigations.

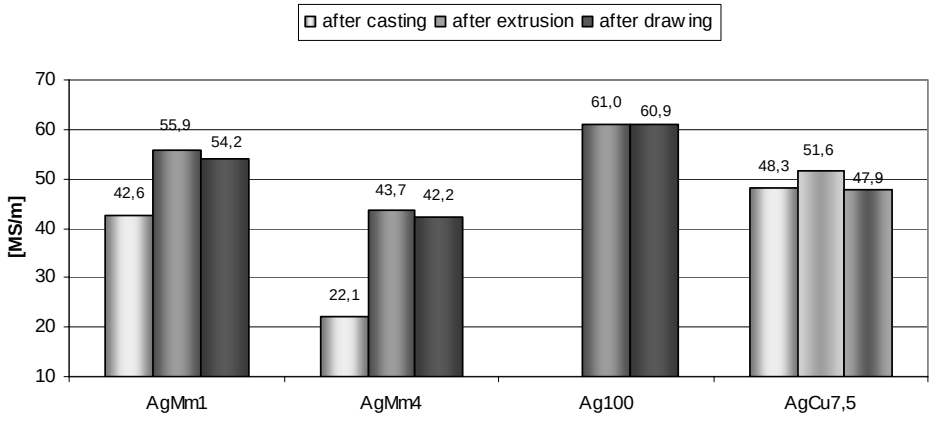


Fig. 7. Electrical conductivity of investigated materials after casting, after extrusion and after drawing

References

[1] J. Stobrawa, Z. Rdzawski, Changes for the development of silver and its alloys manufacturing, Ores and Nonferrous Metals R49/12 (2004).

[2] W. Głuchowski, Z Rdzawski, Silver alloys with enhanced properties, Proceedings of the 6th Conference "Noble metals", Zakopane, 2005, 55-60

[3] W. Głuchowski, Microstructure and properties of new silver alloys dispersion hardened, Proceedings of the 33ed School of Materials Engineering, Kraków-Ustroń, 2005 77-84.

[4] Z. Rdzawski, J. Stobrawa, Improvement of microstructure stability in the PtRh10 alloy for high temperature application, Proceedings of the 13th "European Microscopy Congress" EMC-2004, Antwerp, 2004, MS.12P30 3 667.

[5] Z. Rdzawski, J. Stobrawa, Microstructure and properties of the new Pt-Rh base alloys for high temperature applications, Journal of Materials Processing Technology 153-154 (2004) 681-687.

[6] Z. Rdzawski, J. Stobrawa, J. Szynowski, Microstructure stability of the PtRh alloys used for catalytic ammonia oxidation, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 106-114.

[7] J. Stobrawa, Z. Rdzawski, Precipitation mechanism of the Ni_3Al phase in copper-based alloys, Journal of Achievements in Materials and Manufacturing Engineering 15 (2006) 21-26.

[8] J. Stobrawa, Z. Rdzawski, Deformation behavior of dispersion hardened nanocystalline copper, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 153-156.

[9] J. Stobrawa, Z. Rdzawski, Designing of stable microstructure in material based on the cooper, Polish Metallurgy in 2002-2006, Comitette of Metalurgy PAN, 2006, 51-58.

[10] J. Stobrawa, Z. Rdzawski, W. Głuchowski, Structure and properties of dispersion hardened submicron grained copper, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 195-198.

[11] J. Stobrawa, Z. Rdzawski, Dispersion – strengthened nanocystalline copper, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 35-42.

[12] J. Stobrawa, Z. Rdzawski, W. Głuchowski, Microstructure and properties of nanocystalline copper-ytria microcomposites, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 83-86.

[13] W. Głuchowski, Z. Rdzawski, Stability of properties In silver-lanthanum alloy, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 103-106.

[14] W. Głuchowski, Z. Rdzawski, Silver –mishmetal alloy for application at elevated temperature, Journal of Achievements in Materials and Manufacturing Engineering 26/2 (2008) 123-126.

[15] W. Głuchowski, Z. Rdzawski, Thermal stability of properties in silver-rare earth metals alloys, Journal of Achievements in Materials and Manufacturing Engineering 28/2 (2008) 143-150.

[16] U. Grundmann, M. Hailmaier, L. Schultz, High temperature deformation behaviour of mechanically alloyed microcrystaline ODS silver, Scripta Materialia 37/1 (1997) 103-109.

[17] D.V. Kudashov, H. Baum, U. Martin, M. Heilmaier, H. Ottel, Microstructure and room temperature hardening of ultra fine grained oxide-dispersion strengthened copper prepared by cryomilling, Materials Science and Engineering A387-389 (2004) 768-771.

[18] M. Nganbe, M. Heilmaier, Modelling of particle strengthening in the γ' and oxide dispersion strengthened nickel-base superalloy PM3030, Materials Science and Engineering A387-389 (2004) 609-612.