

Silver – mishmetal alloy for application at elevated temperature

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Materials

ABSTRACT

Purpose: The aim of this work was to investigate the changes taking place in the structure and properties of silver - mishmetal 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 samples obtained by melting and casting in an induction furnace. Further plastic working included KOBO® extrusion process and drawing. The mechanical properties (at a room temperature, elevated temperature and after annealing) and microstructure were examined (by the optical, scanning and transmission electron microscopy).

Findings: Structure of the extruded material was fine and homogenous. The alloys with an addition of mishmetal had high electrical conductivity, which was decreasing with an increase in the content of alloy additives. Examination of the mechanical properties has shown that these alloys exhibited (after annealing) an increased stability of properties at elevated temperatures.

Practical implications: The alloy with an addition of mishmetal could be considered, after further investigations, as a material suitable for use in the production of electrical or electronic parts operating at elevated temperature or exposed to temperature changes.

Originality/value: This work demonstrated that properties of the newly designed silver alloys with an addition of mishmetal exhibit temperature stability. The wire made from this material could be easily produced by the developed processing methods, without the need to use annealing operations. Due to the stable properties and excellent electrical conductivity, this alloy is suitable for use in the production of an advanced electrical or electronic equipment.

Keywords: Metallic alloys; Functional materials; Metallography; Electrical conductivity

1. Introduction

Most of the world silver consumption is in electronic and electrical industry (40% in 2003), most often as conductors and contacts [1,2]. Some of them are designed for operation at elevated temperatures or are exposed to periodic temperature changes. Pure silver cannot be used for these applications because of its insufficient mechanical properties and low softening temperature [3,4].

Suitable mechanical properties can be obtained when alloy additives are used, particularly such which cause precipitation hardening [5-12] or dispersion hardening [13-15]. However, this results in a decrease of electric conductivity and very often in a decrease of tarnish resistance.

It is expected that an addition of mishmetal to silver based alloys may contribute to grain size refinement. Due to the presence of hard intermetallic phase particles, this structure

causes an improvement in mechanical properties. The presence of particles in grain boundaries slows down their migration and grain growth. Therefore, the fine-grained structure should be stable at elevated temperatures making these materials suitable for application at elevated temperatures.

2. Experimental procedure

Tests were made with the Ag + (1% wt) mishmetal (AgMM1), Ag + (4% wt) mishmetal (AgMM4) and Ag + (7.5% wt) Cu (sterling) alloys. Ingots were prepared by typical melting and alloying in an open-air induction furnace under the charcoal cover, followed by casting into graphitoid mould. Another comparative material (except sterling) was pure silver (Ag100) prepared by powder metallurgy methods. Because of the assumption 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 on oscillatory turning die press (KOB0). The samples were not heated before extrusion. The reduction degree after extrusion amounted to $S_0/S_1=178$, 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 KOB0 press it was decided to perform further processing by drawing, without any annealing operations. As a result, the wire Φ 1,45 mm in diameter was obtained from an Φ 40 mm ingot ($S_0/S_F=761$, $\ln(S_0/S_F)=6.64$) without any annealing process.

Microstructure of the obtained wire was examined using 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°C. The samples were kept in a given temperature for 30 minutes before the test.

Mechanical properties of 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.

The wire Φ 3 mm was used to prepare samples for electric contacts simulation test covering up to 200000 electric contact cycles under 500V-20A current.

3. Results and discussion

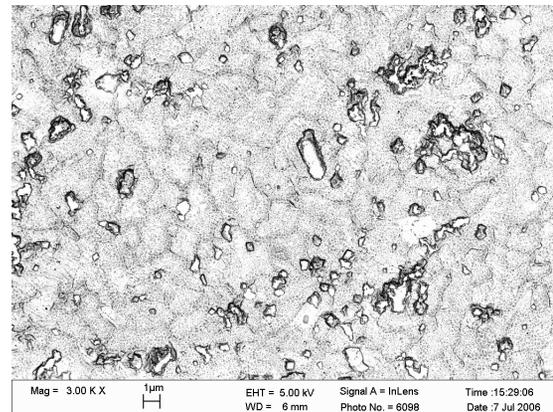
Significant changes in a microstructure obtained after extrusion, compared to the dendritic structure after casting, were observed. The particles had a globular shape and their diameter on a cross-section was within a range of 2-3 μ m. These particles were uniformly distributed within a matrix. Size of the particles obtained after drawing ranged from 0.5 to 2 μ m. 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 μ m, and for a pure silver in range of 10-20 μ m). It should be emphasized that the 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.1).

After annealing (Fig.2) beginnings of recrystallisation process were observed, whereas the pure silver samples were already fully recrystallised.

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 (Fig.3 and 4).

a)



b)

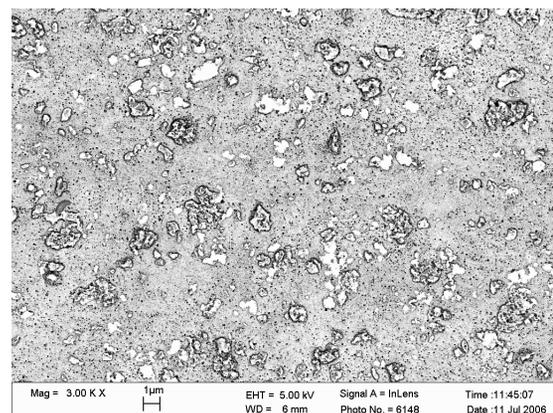


Fig. 1. Images of the structure obtained after drawing, cross-section, etched sample, magn. 3000x: a) AgMM1, b) AgMM4

Mechanical properties of cold worked pure silver decrease considerably at the annealing temperature of 150°C and above (Fig.5). Mechanical properties of the silver-mishmetal alloys, however, remain 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 tension tests performed at elevated temperature (Fig.6) seems to be shifted towards lower temperatures in comparison to the curves in Fig. 5. However, the curves for pure

silver look very similarly in both cases. The yield point of the silver-mishmetal and Ag+7.5Cu alloys measured during tension test at the temperature of 250°C and above had a similar value of about 200 MPa.

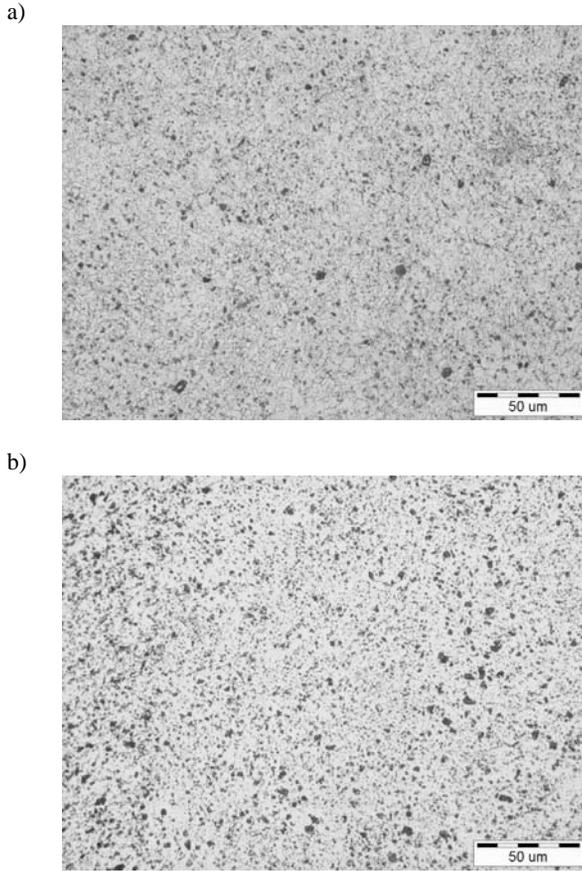


Fig. 2. Images of the structure obtained after annealing 500°C/1h, cross-section, etched sample, magn. 500x: a) AgMM1, b) AgMM4

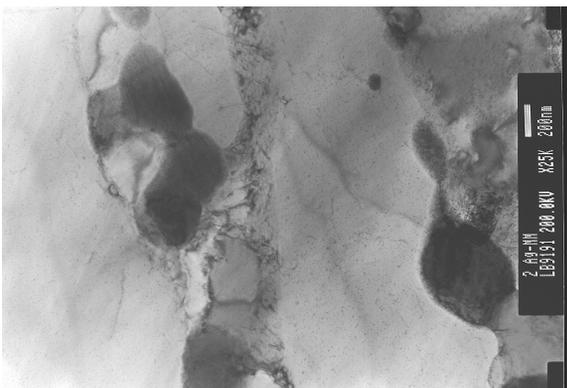


Fig. 3. Microstructure of AgMM1 examined by TEM

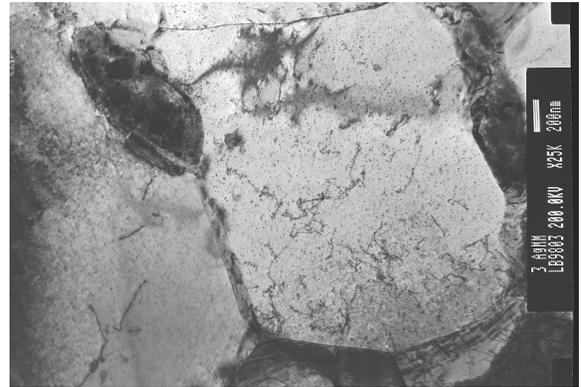


Fig. 4. Microstructure of AgMM4 examined by TEM

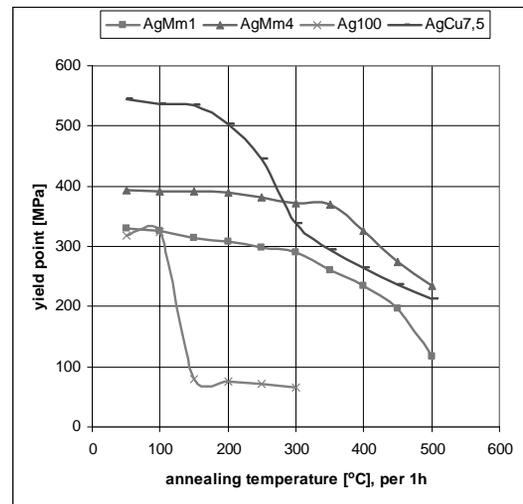


Fig. 5. Tensile strength versus annealing temperature

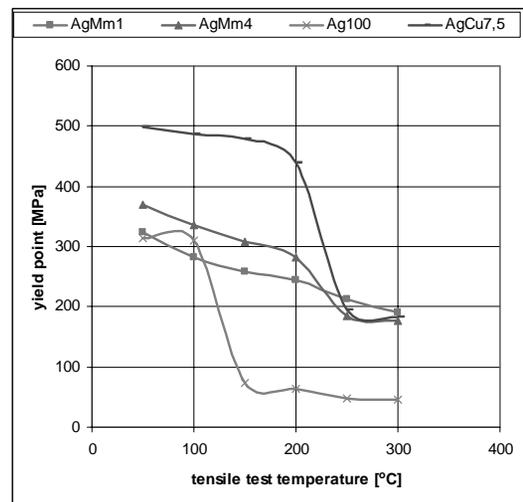


Fig. 6. Yield point versus tensile test temperature.

The highest electrical conductivity after drawing was obtained for pure silver (60.9 MS/m). Conductivity of the silver-mishmetal alloys was decreasing with the increase of alloy additive content (54.2 MS/m at 1% content of mishmetal and 42.2 MS/m at 4% of a mishmetal). Conductivity of the reference Ag-Cu alloy was 47.9 MS/m.

The electric contacts simulation test has shown that the best results, in terms of weight loss and low contact resistance after 200000 switching cycles, were obtained for AgMM1.

4. Conclusions

The microstructure obtained after KOB0[®] extrusion process was fine and uniform. Besides, the size and shape of grains were similar on a cross-section and longitudinal section. The material processing by drawing resulted in further refinement of the structure. Particles on longitudinal sections formed the bands coinciding with the extrusion and drawing directions.

Electron transmission microscopy observations have revealed the presence of particles 200-400 nm in diameter, which probably beneficially influence the mechanical properties and their stability.

Examination of the mechanical properties of the studied alloys has shown that they exhibited after annealing an increased stability of properties at elevated temperatures.

It has been concluded that the alloy with an addition of 1% of mishmetal can be used in the production of electric or electronic parts which are not designed to work under heavy loads but at elevated temperature or can be exposed to temperature changes. It is worth mentioning that mechanical properties of this alloy 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 alloy with an addition of 4% of mishmetal could be used in producing parts which can be exposed to greater temperature changes (above 300°C). Although this alloy has lower electrical conductivity than AgCu7.5, it exhibits better mechanical properties at the temperatures above 300°C.

Further studies are required in order to explain strengthening and properties stabilization phenomena in the silver – mishmetal alloys.

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References

- [1] J. Stobrawa Z. Rdzawski, Silver-perspectives-applications, Proceedings of the V Conference Noble Metals Zakopane-Koscielisko, 2004, 74-81 (in Polish).
- [2] J. Stobrawa, Z. Rdzawski, Prospects of the development silver processing sector, Ores and metals 49/12 (2004) 633-636 (in Polish).
- [3] L.A. Dobrzański, Fundamentals of material science and physical metallurgy, WNT, Gliwice-Warszawa, 2006.
- [4] W. Głuchowski, Z. Rdzawski, Stability of properties in silver lanthanum alloy, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 103-106.
- [5] L. Benner, T. Suzuki, K. Meguro, S. Tanka, Precious Metals Science and Technology, IPMI, 1991.
- [6] I. Kawashimaa, H. Ohnoa, N.K. Sarkar Effect of Pd or Au addition on age-hardening in AgMn-based alloys Dental Materials 16 (2000) 75-79.
- [7] E. Nisaratanaporn, S. Wongsriuksa, Study on the microstructure, mechanical properties, tarnish and corrosion resistance of sterling silver alloyed with manganese, Materials Science and Engineering A445-446 (2007) 663-668.
- [8] M. Banerjee S. Datta, Effect of cold work and trace rare-earth additions on the aging behavior of Al-Cr alloys containing zirconium, Materials Characterization 44 (2000) 277-284.
- [9] S. Hong A. Hill, Microstructural stability and mechanical response of Cu±Ag microcomposite wires, Acta Materialia 46/12 (1998) 4111-4122.
- [10] 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.
- [11] S.B. Youssef, Resistometric study of Ag-8 at% Cu alloy aged in the temperature range 0,4-0,65 T_m, Physica B 228 (1996) 337-341.
- [12] Hyo-Joung Seol, Doun-Hun Lee, Age-hardening and related phase transformation in an experimental Ag-Cu-Pd-Au alloy, Journal of Alloys and Compounds 407 (2006) 182-187.
- [13] J. Stobrawa, Z. Rdzawski, Deformation behavior of dispersion hardened nanocrystalline copper, Journal of Achievements in Materials and Manufacturing Engineering, 17 (2006) 153-156.
- [14] U. Grundmann, M. Gerner, Deformation behaviour of oxide-dispersion-strengthened silver, Materials Science and Engineering A234-236 (1997) 505-508.
- [15] U. Grundmann, M. Heilmaier, L. Schultz, High temperature deformation behaviour of mechanically alloyed microcrystalline ODS silver, Scripta Materialia 37/1 (1997) 103-109.