A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 52 2007 Issue 4

J. GRYZIECKI * J. SOBOTA*

STRUCTURE AND PROPERTIES OF PRECIPITATION STRENGTHENED SILVER ALLOYS

STRUKTURA I WŁAŚCIWOŚCI STOPÓW SREBRA UMOCNIONYCH WYDZIELENIOWO

The paper presents the results of investigations of designed and manufactured silver alloys with additions, enabling by way of precipitation strengthening to obtain high strength properties and such additions which have high negative oxidation energy. In the manufactured alloys a high strengthening effect has been obtained as a result of the precipitation of Al_4Cu_9 phase during the decomposition of supersaturated solid solutions. On the other hand, the alloy additions with high negative oxidation energy formed a self-restoring oxide layer, protecting effectively against atmospheric corrosion. The composition of the obtained properties of the examined alloys guarantees good functional properties of the products made from these alloys as well as high aesthetic assets.
Keywords: silver, mechanical properties, corrosion, solid solution, ageing, precipitation strengthening

Praca przedstawia wyniki badań nad zaprojektowanymi i wytworzonymi stopami srebra z dodatkami umożliwiającymi drogę umocnienia wydzieleniowego uzyskać wysokie właściwości wytrzymałościowe oraz takimi, które mają dużą ujemną energię utleniania. Osiągnięto w wytworzonych stopach silny efekt umocnieniowy w wyniku wydzielania się fazy Al_4Cu_9 podczas rozpadu przesyconych roztworów stałych. Natomiast dodatki stopowe o dużej ujemnej energii utleniania utworzyły warstwę tlenkową, samoodnawialną, chroniącą skutecznie przed korozją atmosferyczną. Zespół uzyskanych właściwości badanych stopów zapewnia wytworzonym z nich wyrobom dobre właściwości użytkowe oraz wysokie walory estetyczne.

1. Introduction

Due to its properties silver has become widely applied. It is characterized by beautiful colour, metallic lustre, great ability of plastic deformation, high electric and thermal conductivity, high coefficient of light reflectance, bactericidal properties and many other unique chemical and electromechanical properties [1-3]. The disadvantage of silver are poor strength properties and small resistance to atmospheric corrosion, known as sulphur corrosion.

In order to increase the strength properties silver alloys containing appropriate additions are produced [1-5]. The applied alloy additions must not only induce the increase of the strength properties of the manufactured alloys of the particular fineness of the noble metal, but also guarantee their high deformability and resistance to sulphur corrosion. It has been found that it is very difficult to satisfy these requirements. It is known that alloys in which the alloy additions create solid solutions with silver are the most resistant to corrosion. However silver alloys having the structure of solutions do not demonstrate appropriately high strength properties guaranteeing indispensable functional properties of products made from these alloys.

A widely applied addition, strengthening silver, is copper. It is most often added to silver to increase its strength properties through phase hardening. A copper addition in the amount up to its solubility limit in the solid state in silver, i.e. to 8.8 wt %, offers also the possibility to carry out the process of precipitation strengthening. Silver alloys with copper addition do not attain high strength properties, and their great disadvantage, is that they easily undergo sulphur corrosion [6]. As a result of the action of this corrosion the alloys lose their beautiful, bright, reflective colour and become covered with dark tarnish [1, 2]. The tendency for the occurrence of sulphur corrosion i.e. the darkening of silver alloys containing copper increases with increasing copper content [1].

The object of investigations in the present study were silver alloys which chemical compositions were de-

* FACULTY OF NON-FERROUS METALS, AGH-UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, AL. MICKIEWICZA 30, POLAND

signed to contain both: alloy additions enabling the hardening of the material by way of precipitation strengthening, and such that demonstrate great tendency for passivation of the alloy surface. The oxide layer formed in this way on the alloy surface will protect against sulphur corrosion [6, 7].

2. Material and methods

There have been designed and manufactured silver alloys of first fineness, i.e. containing the minimal amount 92.5 wt % of silver, the remaining content were appropriately selected alloy additions. The chemical compositions of the alloys are given in Table 1. The alloy additions such as copper and aluminium were expected to allow to carry out the process of precipitation strengthening in order to obtain alloys of high strength properties. The addition of indium or gallium was intended to passivate the alloy surface. Figure 1 shows the isothermal cross-section of the equilibrium of the system Ag-Cu-Al [8].

TABLE 1

Chemical composition of the alloys

Designation of the alloy	Amount of the alloy addition in wt %				
	Ag	Cu	Al	In	Ga
AgCuAl	92.83	4.17	2.98	–	–
AgCuAlIn	92.62	3.43	2.41	1.52	–
AgCuAlGa	92.70	3.49	2.50	–	1.40

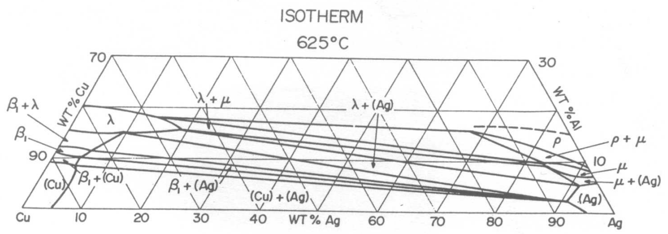

Fig. 1. Isothermal cross-section at 898K of part of the equilibrium system of Ag-Cu-Al [8]

The alloys were prepared using the technique of vacuum metallurgy from components of 99.95% purity. The ingot cast in argon atmosphere were homogenized at 970K and from this temperature solution heat treated by quenching in water. After mechanical treatment they were cold rolled, obtaining the bands. Part of the bands were rolled to the thickness 1.0 mm, and next annealed at 950K for 5 minutes and from this temperature were solution heat treated in water. The remaining part of the bands were rolled to such thickness that after annealing and supersaturation it was possible to give them 30% and 60% reduction, obtaining the thickness of 1.0 mm. The bands of the alloy prepared in this way were the tested material.

Alloys in the supersaturated, and supersaturated and deformed state, were examined in differential scanning calorimeter, heating them at the rate 10K per minute. The structural investigations were carried out using a transmission electron microscope. The value of strengthening during the ageing of the alloys was determined by measuring the mechanical properties obtained from a static tensile test, measurement of Vicker's hardness and Erichsen's drawability test. Investigations of corrosion were carried out in a chamber with a humid atmosphere of SO_2. The SO_2 concentration at the moment of starting the cycle of the investigations was 0.65 dm^3 per 1 m^3 of the chamber. The temperature in the closed chamber was 313K at 90% humidity, and the temperature with the chamber open was 294K. The investigation cycle comprised eight hours of the samples exposition in a closed chamber and next their drying at the chamber doors open for 16 hours. The total duration of the investigations was 9 cycles each of twenty-four hours (216 hours). After each cycle of investigations the changes of the weight of the sulphured samples were determined. Samples of the examined alloys intended for the investigation of sulphur corrosion were in a precipitation strengthened state.

3. Investigation results

The investigations carried out using the differential scanning calorimeter have shown that in all the examined alloys there occur phase transitions. They are documented by the energetic effects recorded on the DSC curves in the course of heating (Fig. 2). On the DSC curves of all the examined silver alloys, both supersaturated and supersaturated and next deformed, there appear very distinct, sharp exothermal peaks with their maximum within the temperature range 523-553K. The maximum of the peaks of supersaturated alloys are shifted to higher temperature by about 10K in relaxation to the maximum of peaks of the alloys supersaturated and afterwards deformed (ε = 30 and 60%).

The processes occurring during the decomposition of supersaturated and supersaturated and next deformed silver alloys induced very great significant changes in the samples strengthening. In Fig. 3 the curves A illustrate the changes of hardness with the duration of ageing of previously solution heat treated alloys. These alloys at first become strengthened very intensely and quickly – within a few minutes. Their hardness increases more than twice. Longer duration of ageing induces farther, however not so intensive increase of hardness. After about two hours of ageing the alloys attain the high, maximum

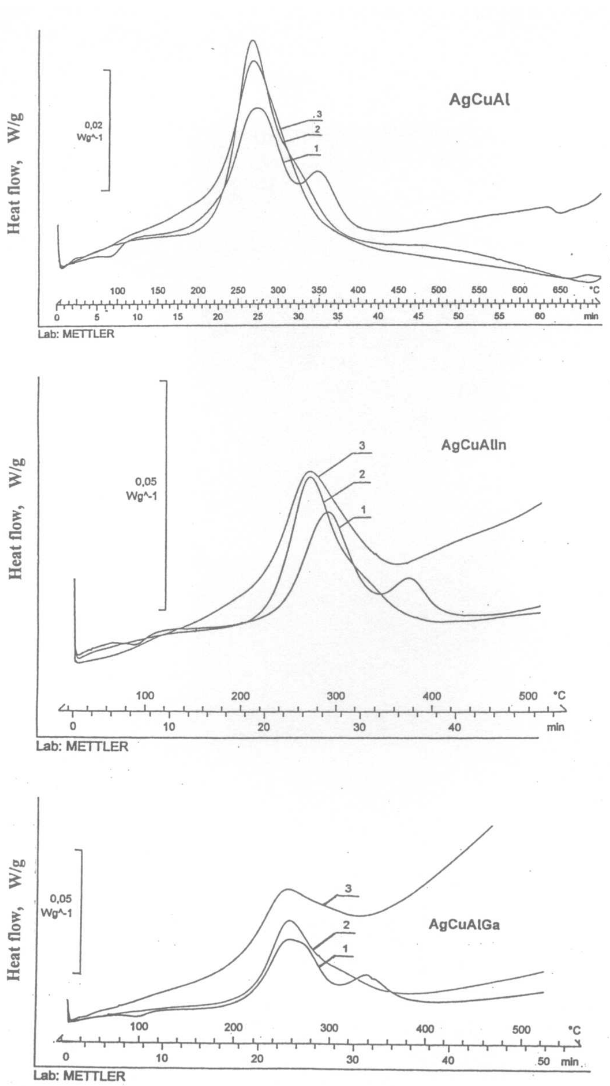

Fig. 2. Calorimetric curves of the alloys: AgCuAl, AgCuAlIn, AgCuAlGa after: 1) solution heat treatment, 2) solution heat treatment and deformation by ε = 30%, 3) solution heat treatment and deformation by ε = 60%

hardness which in the course of further ageing demonstrates great stability. Ageing of alloys which after supersaturation were additionally cold deformed and next subjected to ageing (curves B and C) caused further and still greater increase of hardness.

For the particular states of the examined alloys there have been determined their mechanical properties, listed in Table 2. All alloys in the supersaturated state are characterized by very high ability for plastic deformation, which is evidenced by their great total elongation (A_5) and high value of Erichsen's deformability index (IE_{14}). On the other hand, their strength properties are small. The process of ageing caused very quick and strong strengthening, and as a result the alloys attained very high strength properties and great hardness. Simultaneously, the ability for plastic deformation decreased. Application of thermal plastic treatment caused still greater increase of the strength properties. The greater was the plastic deformation of a supersaturated solid solution, the higher was the increase of the strength properties as the result of ageing.

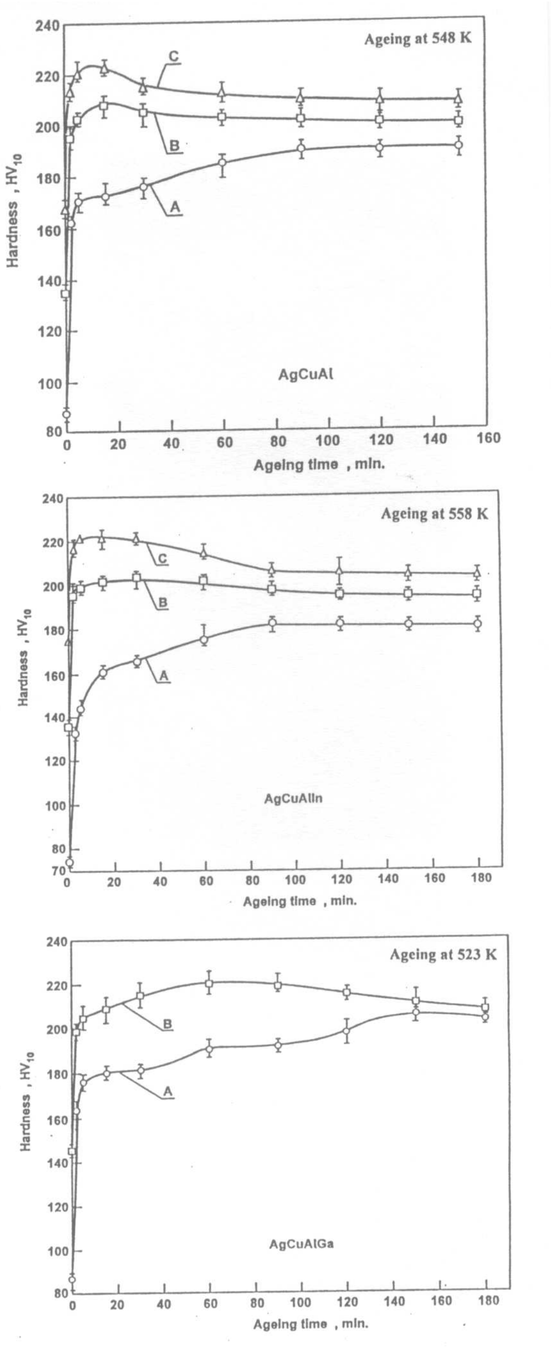

Fig. 3. Changes in the hardness HV10 with the duration of ageing of AgCuAl, AgCuAlIn, AgCuAlGa alloys after: 1) solution heat treatment, 2) solution heat treatment and deformation by ε = 30%, 3) solution heat treatment and deformation by ε = 60%

The level of the mechanical properties of the examined alloys might be also influenced by the alloy additions such as indium and gallium which have been introduced to protect the alloys against sulphur corrosion.

TABLE 2

Mechanical properties of the examined alloys

Type of treatment	Mechanical properties				
	$R_{0,2}$ MPa	R_m MPa	A5 %	HV_{10}	IE_{14}
AgCuAl alloy					
1	2	3	4	5	6
Solution heat treated	175	358	55	80	6.5
Solution heat treated and deformed by ε = 30%	285	480	14	140	–
Solution heat treated and deformed by ε = 60%	335	670	7	165	–
Solution heat treated and aged in 548K for 80 min.	425	585	15	192	–
Solution heat treated, deformed by ε = 30% and aged in 548K for 15 min.	480	677	6	210	–
Solution heat treated, deformed by ε = 60% and aged in 548K for 15 min.	510	720	5	217	–
AgCuAlIn alloy					
1	2	3	4	5	6
Solution heat treated	180	363	59	74	6.6
Solution heat treated and deformed by ε = 30%	290	462	21	135	–
Solution heat treated and deformed by ε = 60%	342	593	8	175	–
Solution heat treated and aged in 558K for 90 min.	398	571	16	182	–
Solution heat treated, deformed by ε = 30% and aged in 558K for 30 min.	430	648	9	203	–
Solution heat treated, deformed by ε = 60% and aged in 558K for 30 min.	475	694	5	221	–
AgCuAlGa alloy					
1	2	3	4	5	6
Solution heat treated	190	320	52	86	6.8
Solution heat treated and deformed by ε = 30%	272	445	16	146	–
Solution heat treated and aged in 523K for 150 min.	395	576	4	206	–
Solution heat treated, deformed by ε = 30% and aged in 523K for 90 min.	428	638	5	220	–

Their influence on the mechanical properties has been indicated in his investigations by Nada [10]. Investigations carried out by this author indicate the increase of the flow stress in AgCu2 alloy deformed in a wide range of temperature as a result of introducing the addition of 0.5 wt% of indium. According to Nada [10] it can be attributed to the phenomenon of segregation of indium atoms to the grain boundaries, which in this way become more difficult obstacles for the movement of dislocations.

It must be also taken into consideration that alloy additions such as aluminium, indium and gallium considerably reduce the stacking fault energy (SFE) of silver [11]. SFE reduction in the alloy limits the ability of the perfect dislocations to dissociation into partial dislocations, which as a consequence makes impossible the occurrence of transverse slip, resulting in the strengthening of the material.

The performed structural observations indicate that intensive increase of the work hardening of the examined alloys which occurred in the ageing process is due to the precipitations of the coherent phase λ (Al_4Cu_9). This phase has a regular, complex structure of the type of brass γ of $D8_2$ lattice [8]. In the initial period of ageing the phase precipitations are small with the shape similar to disc of the diameter from 20 to 60 nm. The precipitations are distributed uniformly in the whole volume of the alloy. Figures 4 and 5, respectively show the precipitations of the Al_4Cu_9 phase in AgCuAlIn alloy,

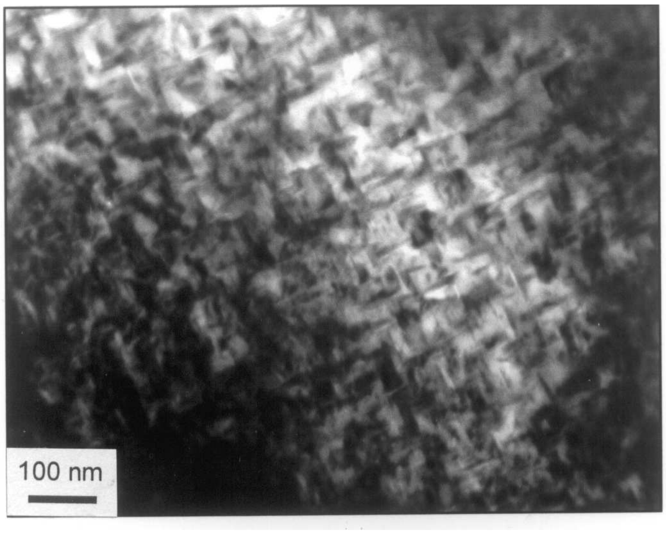

Fig. 4. Microstructure of AgCuAlIn alloy aged at 558K for 90 minutes

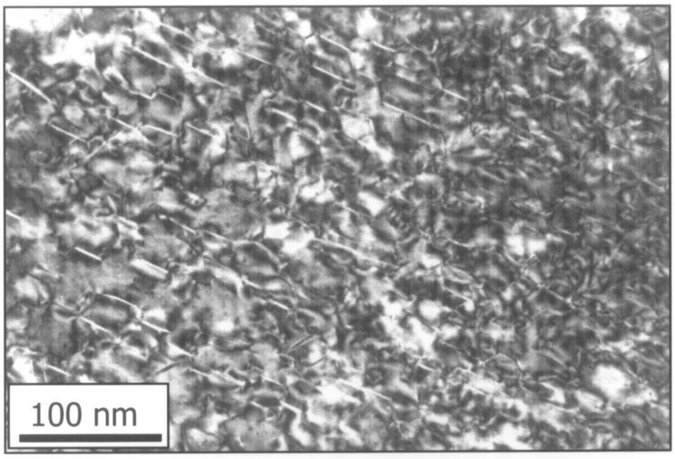

Fig. 5. Microstructure of AgCuAlGa alloy aged at 523K for 90 minutes

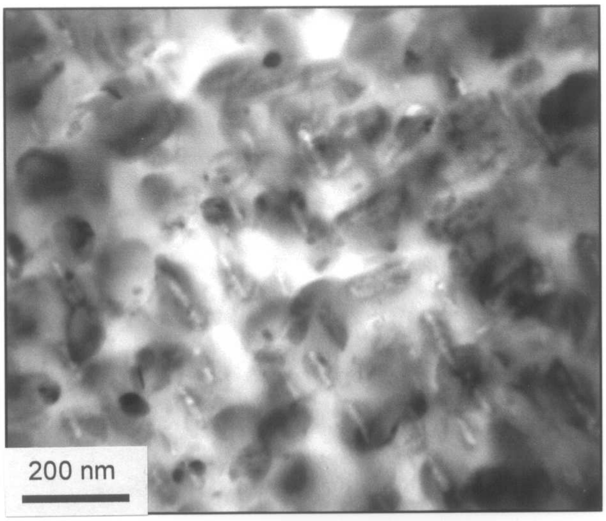

Fig. 6. Microstructure of AgCuAlIn alloy aged at 558K for 140 minutes

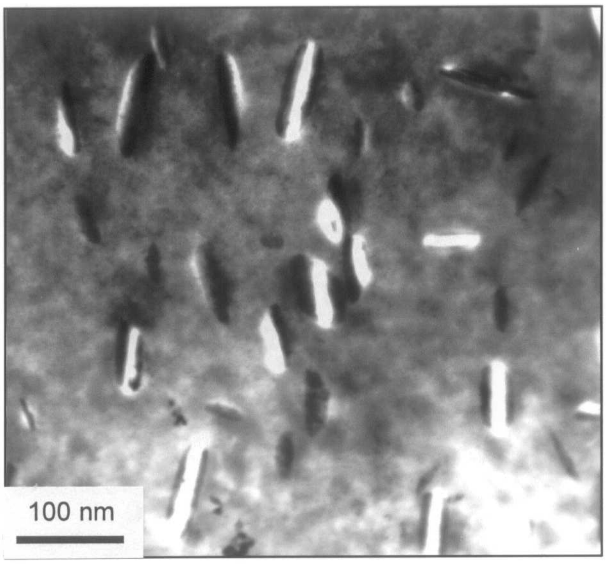

Fig. 7. Microstructure of AgCuAlGa alloy aged at 523K for 180 minutes

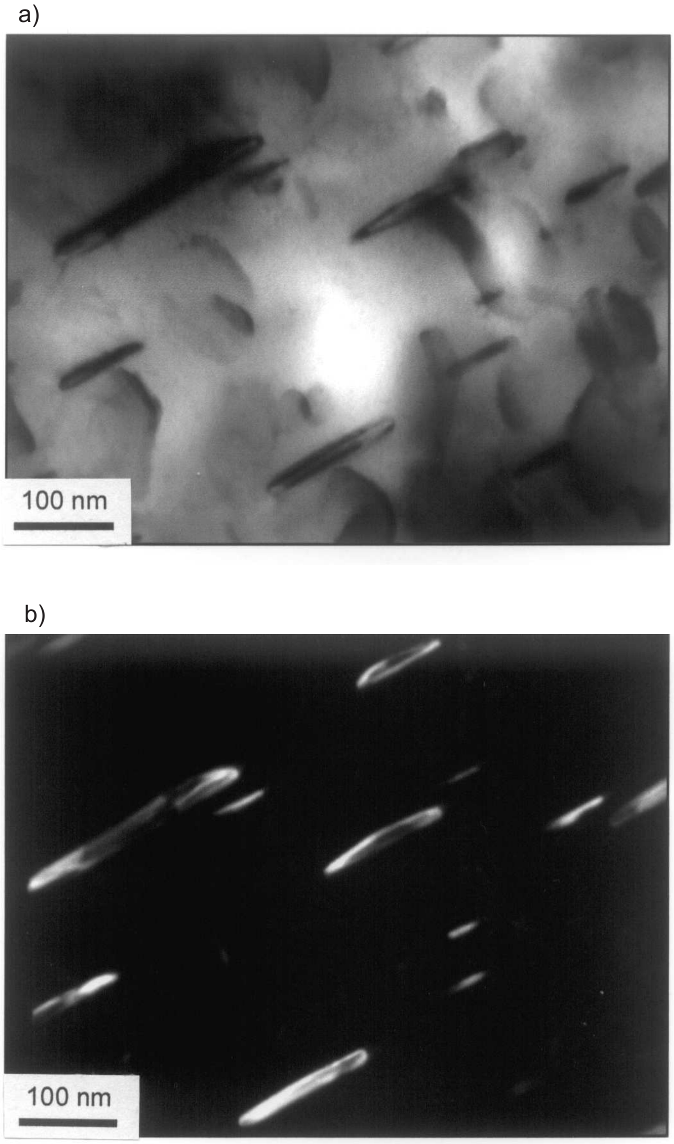

Fig. 8. Microstructure of AgCuAlIn alloy aged at 558K for 1400 minutes, a) observation in a bright field, b) observation in a dark field

aged at 558K and in AgCuAlGa alloy, aged at 528K. The time of ageing of both these alloys was 90 minutes. Longer time of ageing causes the growth of precipitations. Precipitations of Al_4Cu_9 phase in AgCuAlIn alloy after 140 minutes, and in AgCuAlGa alloy after 180 minutes of ageing attain the size of 80÷100nm. The precipitations are in a clear contrast with the stress fields, symmetrical on both sides, formed in the matrix of the alloys (Fig.6, 7). Such a picture of the precipitations together with the contrast derived from the stresses is defined as "coffee grains". Ashby and Brown [9] have demonstrated that the observed contrast from the stress fields is induced by the deformation of the alloy matrix by the precipitations which have been formed. It is an effect of the "vacancy type". After a very long time of ageing the deformation contrast around the precipitations is not observed which is evidence of the loss of coherence (Fig. 8a, b).

Alloys solution heat treated and deformed, and afterwards aged attain high properties as a result of both precipitation strengthening as well as, to a great extent, deformation strengthening. Structural investigations of alloys after thermo-mechanical treatment made visible the strengthening precipitations of the Al_4Cu_9 phase, very thin deformation twins and the cellular dislocation systems. Figures 9 and 10 show the deformation twins and precipitations of Al_4Cu_9 phase in AgCuAlIn and AgCuAlGa alloys. The newly formed dislocations during plastic deformation of a supersaturated solution become reorganized during ageing, forming cellular systems. The cellular dislocation systems formed in aged AgCuAlIn and AgCuAlGa alloys are shown in Figs 11 and 12.

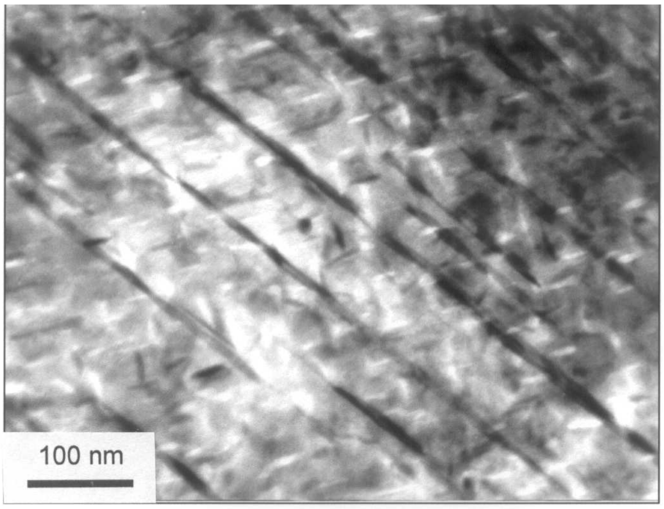

Fig. 9. Microstructure of AgCuAlIn alloy solution heat treated and deformed by ε = 30% and next aged at 558K for 30 minutes

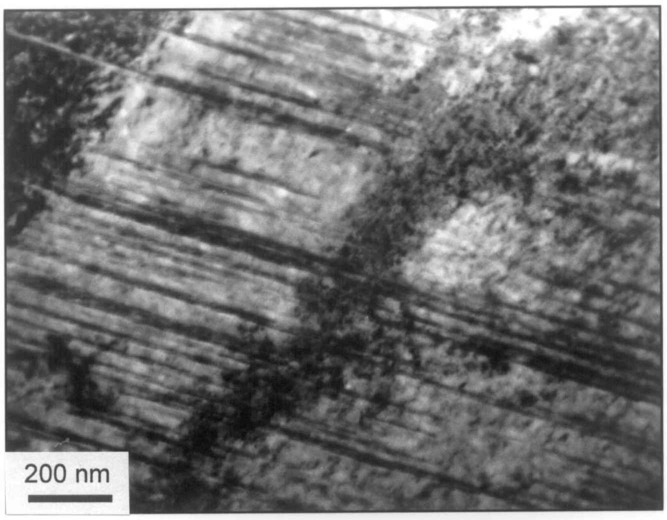

Fig. 10. Microstructure of AgCuAlGa alloy solution heat treated and deformed by ε = 30% and next aged at 523K for 80 minutes

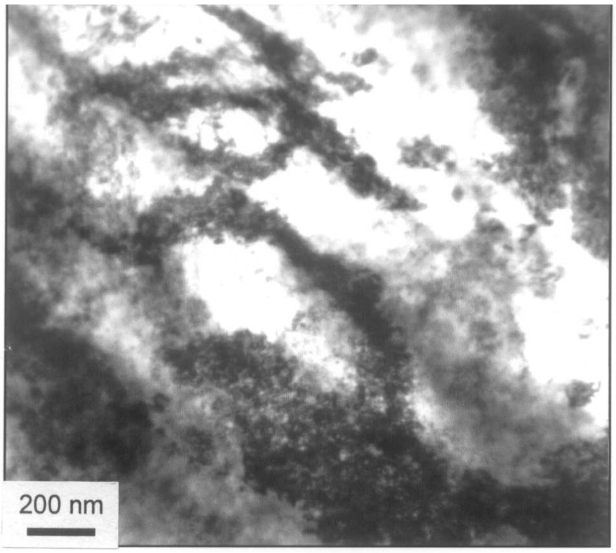

Fig. 11. Microstructure of AgCuAl alloy solution heat treated and deformed by ε = 30% and next aged at 548K for 60 minutes

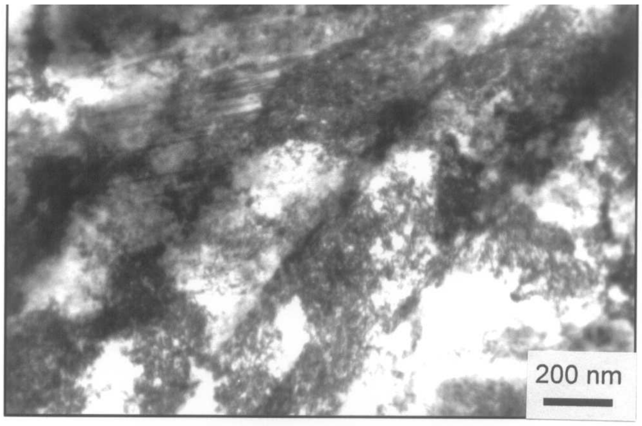

Fig. 12. Microstructure of AgCuAlGa alloy solution heat treated and deformed by ε = 30% and next aged at 523K for 80 minutes

The results of the conducted laboratory investigations of corrosion in the atmosphere of sulphur dioxide with humidity condensation are shown in Fig. 13. It represents the elementary mass changes as a function of the cycles of sulphuring as well as their duration of alloys which were the object of the investigations as well as of widely used jewellery silver alloy with 7.5 wt% of copper. In the initial period of sulphuring, i.e. up to the fifth cycle, the changes of the mass of the designed alloys is very small. Further sulphuring cycles do not induce any increase of the mass. On the other hand, a considerable increase of the mass during sulphuring takes place in the jewellery alloy AgCu7.5. The increase of the mass of this alloy is very great already from the first cycle of sulphuring. Observations of the surface of the designed alloys, carried out after the sulphuring process, have revealed that they have lost their reflectance only a little, whereas the change of the surface of AgCu7.5 alloy was very noticeable. This surface was covered with tarnish and changed its colour into grey.

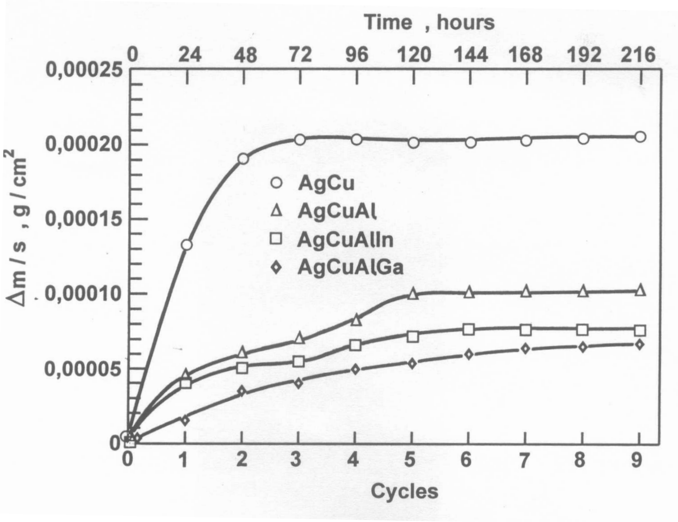

Fig. 13. Elementary mass changes of AgCuAl, AgCuAlIn, AgCuAl-Ga alloys and the jewellery alloy AgCu7.5 as a function of the cycle (duration) during the corrosion resistance in humid atmosphere, containing SO_2

When analysing the effects of sulphuring the examined alloys there can be noticed a strong anticorrosion action of the alloy additions, such as In, Ga and Al. The alloys, containing these elements, due to the protective oxide layer of these metals formed on the surface of the samples, have shown great resistance to corrosion. The lack of the protective layer in the jewellery alloy AgCu7.5 is responsible for the fact that this alloy is very susceptible to corrosion.

4. Summarizing remarks

The obtained investigation results have shown that the manufactured new silver alloys, with appropriate amounts of alloy additions, such as Cu, Al, In or Ga, are characterized by very high strength properties after ageing and great ability for plastic deformation in the supersaturated state. Application of thermo-mechanical treatment enabled still greater increase of the work-strengthening of the alloys. This strong strengthening effect in the alloys is the result of the precipitation of Al_4Cu_9 phase during the decomposition of the supersaturated alloy. The strengthening process proceeds very quickly and the acquired properties show great stability with the duration of ageing. The strength properties of the examined alloys not only exceed almost twice the properties of the jewellery alloy (AgCu7.5) of 925 fineness, but even those of the alloy of 800 fineness (AgCu20). Moreover, these alloys are characterized by very good resistance to sulphur corrosion due to the formation of a protective layer from the oxides of the alloy additions on the alloy surface. The applied protection against corrosion shows the advantage that in case of damage of the oxide layer as a result of scratch or abrasion, it quickly undergoes self-induced restoration.

Both the high mechanical properties and very good corrosion resistance of the produced alloys make them a valuable, jewellery material, especially for the production of large shell goodies, such as jars, trays, sugar bowls, silver plates, etc.

Acknowledgements

The work was realized in the grant project No. 3 T08 B 01829.

REFERENCES

[1] W. Babiński, Srebro i jego zastosowanie, Wydawnictwo Politechniki Śląskiej, Gliwice (1986).
[2] B. M. Małyszew, D. B. Rumiancew, Srebro, Metallurgia, Moskwa (1976).
[3] W. Głuchowski, Z. Rdzawski, VI Konf. Metale Szlachetne, 73 (2005).
[4] J. Stobrawa, Z. Rdzawski, Rudy i Metale Nieżelazne **12**, 633 (2004).
[5] M. Meretukow, A. Orlow, Metallurgia Błagorodnych Metallow, Wyd. Metallurgia, Moskwa (1991).
[6] S. Mrowec, T. Werber, Korozja gazowa tworzyw metalicznych, Wyd. "Śląsk", Katowice (1965).
[7] M. F. Ashby, D. R. H. Jones, Materiały inżynierskie, Wyd. Naukowo-Techniczne, Warszawa 242 (1995).
[8] Y. A. Chang, D. Goldberg, J. P. Neumann, Journal of Physical and Chemical Reference Data **6**, 626 (1977).
[9] M. F. Ashby, L. M. Brown, Phil. Mag. **18**, 1083 (1963).
[10] R. H. Nada, Physica B 349, 166 (2004).
[11] P. C. J. Gallagher, Metallurgical Trans. **1**, 2429 (1970).

Received: 15 March 2007.