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SILVER ALLOYS RESISTANT TO DARKENING

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The study presents the results of investigation of the resistance to sulfur corrosion and of the mechanical properties of silver alloys without copper, of 925 fineness. As the alloy additions there were used elements which are able to create on the alloy surface an oxide layer as a protection against corrosion and which reduces the SFE of the alloy. The obtained silver alloys without copper, of 925 fineness, are characterized by high resistance to the action of sulfur corrosion and good mechanical properties.

Keywords: silver, alloy, corrosion, mechanical properties, solid solution

W niniejszej pracy przedstawiono wyniki badań odporności na działanie korozji siarkowej oraz właściwości mechanicznych bezmiedziowych stopów srebra próby 925. Jako dodatki stopowe zastosowano pierwiastki, które mają zdolność do tworzenia na powierzchni stopu warstwy tlenkowej, stanowiącej ochronę przed korozją oraz obniżające EBU stopu. Wytworzone bezmiedziowe stopy srebra próby 925 cechują się bardzo dobrą odpornością na działanie korozji oraz dobrymi właściwościami mechanicznymi.

1. Introduction

Silver belongs to metals known already in ancient times. Beautiful white colour, metallic lustre, great ability for plastic deformation made silver, besides gold, a metal used for the production of various types of jewellery, objects of artistic handicraft as well as everyday use. The development of production technology extended the area of silver application due to its high electric and thermal conductivity, high coefficient of light reflection, bactericidal properties and many other chemical and electrochemical properties [1-3]. The application of pure silver is limited by its low strength properties. To increase these strength properties various alloy additions are used. The most often applied alloy addition is copper. Silver alloys containing from 7,5 to 20 wt% of copper are produced on a wide scale. They are used for the production of jewellery articles, ornaments, coins and shell products, such as jars, plateaus, sugar bowls, candlesticks, etc. Copper addition to silver gives a two-phase alloy, little resistant to sulfur corrosion.

The resistance of silver alloys to corrosion is one of the important properties which in many cases determines their application. As a result of the action of sulfur corrosion the products made from silver, and especially those made of silver alloys with copper, become covered with dark, unpleasant tarnish, which is the result of silver reaction with sulfur, the source of which is the hydrogen sulfide H_2S and sulfur dioxide SO_2. These compounds are present in the atmosphere, in food articles and in many chemical products. The products of corrosion are Ag_2S and Ag_2SO_4 [4-7]. Besides this, SO_2 reacts with silver admixtures, such as represented by copper, creating the sulfide Cu_2S. Oxygen can also react with copper, creating Cu_2O. In this way on the alloy surface forms a thin layer, containing besides Ag_2S and Ag_2SO_4, also the copper compounds – sulfide and cupric oxide [3], causing intense darkening. The rate of the occurrence of sulfur corrosion in the alloys of silver with copper increases with the increasing content of copper present in these alloys. In silver alloys, unlike in pure silver, there can be observed the phenomenon of intercrystalline corrosion, occurring on the boundaries of the crystal grains of the particular phases and that of stress corrosion [7].

By introducing determined amounts of appropriate additions into silver, it is possible to inhibit the reactions

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of darkening by way of creating a protective layer on the alloy surface. When adding elements of high oxidation energy to silver it is possible to create a thin layer of the oxide of this element on the alloy surface. If the oxide has protective properties, such as e.g. Al_2O_3, SiO_2, In_2O_3, Cr_2O_3, or BeO, it will inhibit the darkening of the alloy [8]. The advantage of this protective oxide layer is that in case of scratching or wearing it undergoes self-induced restoration.

The present study describes the investigations of silver alloys of fineness 925 without copper as the alloy addition. It has been replaced by appropriately selected components. There have been introduced alloy additions, with the aim to increase both the strength properties and to form on the alloy surface an oxide layer as a protection against corrosion. There have been also carried out investigations of the properties of the commonly used jewellery alloy of 925 fineness, in which copper is the alloy addition. Investigations of the silver with copper alloy were carried out in order to compare its resistance to sulfur corrosion and its mechanical properties with the properties of the proposed new silver alloys.

2. Material and investigations methods

Silver alloys of the first fineness and the chemical composition shown in Table 1 were designed and executed.

TABLE 1

Chemical composition of the alloys

Alloy No	Designation of the alloy	Amount of the alloy addition in wt%					
		Ag	Sn	Al	In	Ga	Cu
1	AgSnAl	93,12	4,08	2,75	–	–	–
2	AgSnIn	92,96	4,86	–	2,18	–	–
3	AgSnAlIn	92,83	4,17	1,45	1,55	–	–
4	AgSnAlGa	93,32	2,75	2,59	–	1,32	–
5	AgCu7,5	92,57	–	–	–	–	7,42

The alloys were made from components of 99,99% purity. The batches were melted in a vacuum induction furnace, in graphite crucibles. The alloys were cast in argon atmosphere, poured into steel moulds, covered with wax. The ingots were homogenized at 973 K for 24 hours in charcoal. Homogenized ingots were mechanically treated and next subjected to cold rolling. The obtained bands, 1,2 mm thick, was annealed with recrystallization at the temperature 820 K for 5 minutes. A number of the recrystallized bands were deformed by rolling, inducing 15 and 30% reduction. From alloys prepared in this way there were cut out samples for the investigations of the mechanical properties and the sulfur corrosion. The mechanical properties were determined in a static tensile test, Erichsen's formability test and by measurements of Vicker's hardness. The investigation of corrosion was carried out in a chamber with humid atmosphere of SO_2. SO_2 concentration at the moment of starting the cycle of the investigation was 0,65 dm^3 for 1 m^3 of the chamber, the temperature in the closed chamber was 313 K at the humidity of 90%; temperature with open chamber door was 294 K. The duration of the investigation cycle was eight hours of the samples exposition in the closed chamber and next their drying with open chamber door for 16 hours. The total time of the investigations comprised 9 cycles of 24 hours (216 hours); after each investigation cycle the changes of the mass of the sulfurized samples were determined.

3. Investigation results and their analysis

Samples from the developed alloys in the form of plates in recrystallized state were subjected to the investigations of corrosion. The grain size in the samples was about 25 μm. The results of investigations of the sulfur corrosion are shown in Fig. 1.

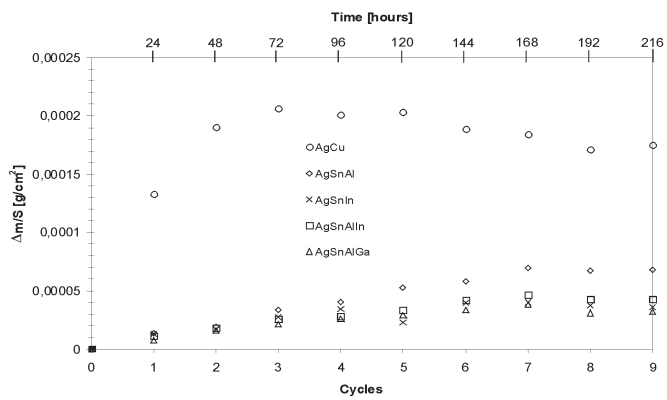

Fig. 1. Elementary mass changes of silver alloys as a function of the number of the cycles (time) of sulfurization in humid atmosphere containing SO_2

It presents the elementary mass changes as a function of the number of the sulfurization cycles as well as the time of both designed and developed alloys, and also of the commonly used jewellery alloy AgCu7,5. Changes of the mass of the designed alloys during sulfurization are small. In the initial period of sulfurization, i.e. up to the fourth cycle, there takes place a small increase of the mass of the alloys. The next cycles of sulfurization do not cause any increase of the mass. An exception is the alloy AgSnAl, which undergoes corrosion in a rather small degree in the subsequent cycles of sulfurization. The presented results are evidence that the examined alloys represent very high resistance to sulfur corrosion, whereas a considerable increase of mass during sulfurization takes place in the jewellery alloy AgCu7,5. The mass increase in this alloy is very great, starting from the first cycle of sulfurization. The increase of the mass of AgCu7,5 alloy is several times greater than the increase of mass in the other alloys. The performed observations of changes on the surface of the alloys samples after sulfurization process show differences in their reflectance and colouring. The surfaces of the alloys AgSnIn, AgSnAlIn and AgSnAlGa lost their lustre only a little. A more noticeable change of the surface is observed in the alloy AgSnAl. Its surface was slightly covered with tarnish, whereas the surface o the alloy AgCu7,5, as a result of sulfurization lost its reflectance, was covered with tarnish and changed its colour into grey.

When analysing the results of sulfurization of the examined alloys one can notice strong anticorrosive influence of the alloy additions, such as In, Ga and Al. Alloys containing these elements, due to the protective layer of the oxide of these metals, formed on the sample surface, showed great corrosion resistance. The absence of the protective layer in the jewellery alloy AgCu7,5 made it very susceptible to the action of sulfur corrosion. The additions introduced into the silver were expected not only to induce good resistance to corrosion, but also to produce proper mechanical properties at a level guaranteeing the possibility of obtaining a definite product with the required useful properties. When designing alloys from components creating a solid solution with silver, it was taken into consideration that materials of this type do not attain high strength properties, since solution strengthening does not induce great work hardening of the alloy. A method which can increase the hardening is to produce alloy of small grain size. This is well documented by the Hall-Petch relation [9]. Investigations of the influence of the grain size on work hardening in silver alloy with 8% addition of copper atoms have been presented by Kenawe [10]. Considering the Hall-Petch relation the process of recrystallizing annealing of the examined alloys was carried out in such a way as to obtain as small grains as it was possible.

When introducing such additions as Sn, Al, In, Ga, consideration was given also to the fact that they will reduce the value of the stacking fault energy (SFE) of silver. Gallagher [11] informs that Sn, In, Al can reduce the SFE of silver from about 20 erg/cm^2 even to 5 erg/cm^2. Reduction of SFE in the material limits the ability of complete dislocations for splitting into partial dislocations, which as a consequence prevents the occurrence of cross slip, thus inducing the work hardening of the material.

The influence of the alloy additions used in the present study on the mechanical properties of the obtained alloys in recrystallized state and deformed by 15% and 30% reduction is shown in Table 2.

TABLE 2

Mechanical properties of silver alloys without copper and AgCu7,5 alloy in the recrystallized state and deformed by 15% and 30% reduction

Alloy	AgSnAl	AgSnIn	AgSnAlIn	AgSnAlGa	AgCu7,5
Alloy No	1	2	3	4	5
Properties of alloys in recrystallized state					
$R_{0,2}$, MPa	115	70	105	85	180
R_m, MPa	310	250	290	260	290
A_5, %	63	70	63	71	40
IE_{14}	6,9	7,2	7,2	7,5	7,3
HV_{10}	70	50	65	58	75
Properties of alloys in the strengthened state, ε_1 = 15%					
$R_{0,2}$, MPa	230	185	220	180	195
R_m, MPa	374	313	350	318	335
A_5, %	38	36	38	45	31
HV_{10}	112	102	113	97	105
Properties of alloys in the strengthened state, ε_2 = 30%					
$R_{0,2}$, MPa	240	215	240	210	250
R_m, MPa	437	349	430	364	387
A_5, %	17	26	13	21	20
HV_{10}	133	117	127	123	121

The examined alloys in the recrystallized state are characterized by very good formability, evidenced by very great total elongation and high drawability. Their tensile strength is comparable with the strength of the jewellery alloy AgCu7,5. Their yield point, however, is lower than that of this alloy. When subjected to 15% and 30% plastic deformation they attain properties comparable with the properties of AgCu7,5 alloy deformed by the same degree.

The obtained investigation results show that elimination of copper addition as an alloy component to silver and replacing it by appropriate amounts of such elements as Sn, Al, Ga, allows to obtain alloys of great resistance to sulfur corrosion and of mechanical properties comparable with the jewellery alloy AgCu7,5.

4. Summarizing remarks

An effective method to obtain silver alloys of high sulfur resistance is elimination of copper as the alloy addition. Copper can be replaced by such alloy additions which are able to form with silver a solid solution and are characterized by the ability to form on the alloy surface an oxide layer as a protection against corrosion. In order to guarantee obtaining the appropriate mechanical properties the recrystallization process should be carried out in such a way as to obtain small grain size. When selecting the alloy additions there should be also considered the possibility of obtaining alloy of low SFE.

The investigations described in the present study have shown that alloy additions such as Sn, Al, In and Ga, offer the possibility to produce silver alloy of 925 fineness, characterized by good mechanical properties and very high resistance to sulfur corrosion. Resistance to the action of sulfur corrosion is many times higher than that of the generally applied jewellery alloy AgCu7,5.

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