



The Effect of Addition of Germanium to the Surface Phenomena in Silver Alloys

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Abstract

The article describes the impact of germanium on the course of surface phenomena in casting alloys of silver used in gold smithing. The aim of this work is to describe the assessment of resulting alloys, comparing the area of raw castings and the impact of the addition content of the alloy on the hardness of the samples. The evaluation also was subject to corrosion resistance of giving a comparison of their use in relations to traditional silver alloys.

Keywords: Silver, Germanium, Microstructure, Oxide layers, Corrosion

1. Introduction

Known since ancient times, silver is the most popular material for use in manufacture of jewelry. Silver for the commercial use contains not less than 99,9% Ag. The remaining 0.1% is a contamination in the form of copper, lead or iron. Pure silver does not have sufficient strength properties and therefore other additions are used to strengthen it. Thanks to this, the alloys increase in strength, hardness and abrasive wear resistance with slightly decrease in ductility.

One of the most known and used silver alloy is the alloy of silver-copper (Ag-Cu) called "Sterling Silver", wherein the copper content is 7.5%, and content of silver is 92.5%. The most serious problem in the described alloy is a surface oxidation. Oxygen in the air combines with copper and form on an surface alloy a black copper oxide (II) (CuO) and reddish-gray subsurface copper oxide (I) (Cu₂O).

Both of these factors affect the reduction of the mechanical properties and the deterioration of the surface quality of the alloy. Silver used for the jewellery cannot have chemical reactions.

The metal-skin contact can cause allergic reactions. Therefore to prevent metal reacting with the environment, electrochemical surface coating with rhodium or ruthenium is carried out. Such processes are called, respectively, rhodium and ruthenium. However, the layers are expose to abrasion. Competitiveness on the jewelry market requires searching for a new material solutions which are attractive to customers and easier to process.

The newly developed silver alloys with alloy additions as: aluminum, germanium, zinc, cadmium or phosphorous do not react with oxygen. They increase the hardness and wear resistance of the alloys meets increased ductility. In the case of the addition of germanium it permits the creation of self renewing oxide layer on the surface, which prevents the spread of corrosion in to the material.

2. Work Methodology

2.1. Preparation of models

In the framework of the research developed three silver alloys with additions of copper and germanium. The silver content of

each alloy was the same, while the content of the other elements was variable (Tab.1). Metal alloys were self-made compositions.

Table 1.

The chemical composition of the alloys

Silver Alloy	Contribution of the elements [% wt]		
	Ag	Cu	Ge
AgCu	Bal.	7	-
AgCuGe1	Bal.	6	1
AgCuGe2	Bal.	5	2

Samples for the implementation of silver casting were made from plate shape wax of 10x20x4 mm. Models were milled and soldered to a wax pin. To prepare the flasks Ronson&Randolph investment powder were used. Then the flasks were burn out In an oven at 550 ° C and held until the casting. Due to the much lower density of germanium in comparison to the density of silver (about twice) and the formation of germanium oxides at elevated temperatures, element was supplied in to the mirror of liquid metal with a special tweezers.

This procedures allow to avoid the described phenomena and insert it into a melted alloy practically with out of losses. Three casting processes were carried out using Yasui K2E vacuum pressure furnace. Metal was melted in graphite crucible with a capacity of about 0.5 kg. Casting process was carried out under a shielding gas, i.e. argon.

2.2. Study of the microstructure and hardness

Metallographic examination was conducted on an optical microscope with the magnification x100, x200 and x500. To reveal the microstructure samples was etched with a solution of 10ml H₂SO₄ with 60g CrO₃ and 100ml H₂O.

Furthermore, in order to determine the distribution of elements in the castings observations with the scanning electron microscope (SEM) with test chemical composition (EDS) were made.

The hardness measurements were made using a Vickers method at a load of 100g. For each sample six measurements were made. However, to minimize the measurement error arising from the uneven distribution of hardness on the surface of a sample, two extreme results were rejected.

2.3. Testing Corrosion Resistance

Samples intended for corrosion tests should have similar structure and topography of the surface that is being analyzed. For this purpose, the samples were abraded with emery board of the same grit and degreased.

Research was performed at 25 ° C in Ringer solution in a three-electrode system. The reference electrode was a saturated calomel electrode. Before the test, in order to stabilize the

corrosion potential the samples were immersed in a corrosive solution for 60 min. Then, the samples were polarized by the potential of approx. 300 mV lower potential to 1500 mV using a modification of the potential of 0.2 mV / s.

Obtained graphs were analyzed using the computer program AtlasLab to determined characteristic of the electrochemical values (corrosion potential, corrosion current density, polarization resistance).

3. Results

Figures 1 and 2 show the structure and microstructure of the resulting casts.

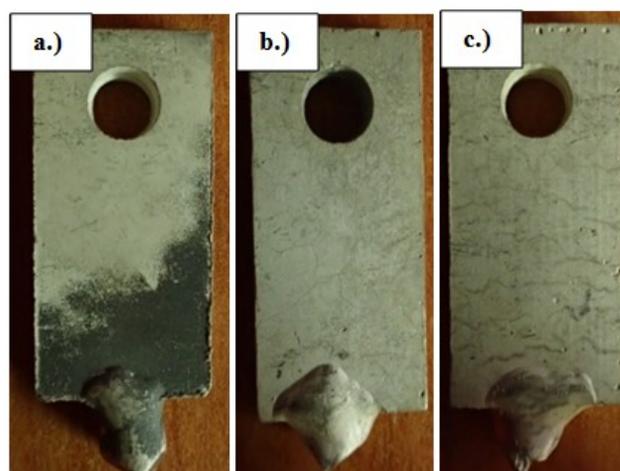


Fig. 1. a) The sample surface of the composition 93%Ag, 7%Cu
 b) The sample surface of the composition 93%Ag, 6%Cu, 1%Ge
 c) The sample surface of the composition 93%Ag, 5%Cu, 2%Ge

The SEM analysis of the cross section of the sample allowed for the disclosure of copper oxides formed on the surface of the AgCu alloy (Fig. 3). Use of the EDS detector, allowed to obtain a decomposition of the elements on the sample cross section. The direction of the study is presented in Fig. 4, while the obtained results of Ag and Cu distribution are presented in Fig. 5.

The SEM microstructure of the cross section of the alloy sample with 1% germanium is shown in Fig. 6, while relevant for the alloy element distribution is shown in Fig. 7.

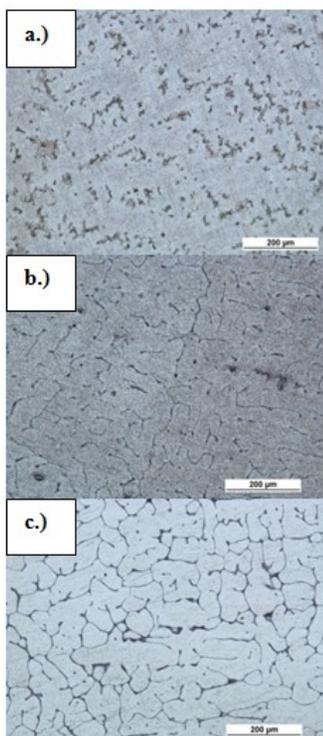


Fig. 2. a) The sample microstructure of the composition 93%Ag, 7%Cu b) The sample microstructure of the composition 93%Ag, 6%Cu, 1%Ge c.) The sample microstructure of the composition 93%Ag, 5%Cu, 2%Ge

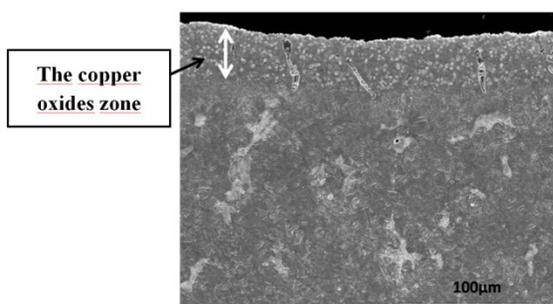


Fig. 3. The microstructure of the AgCu7 alloy, 500x

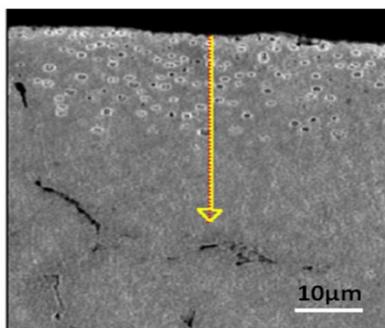


Fig. 4. The direction of the study the chemical composition of the sample cross-section AgCu7 alloy

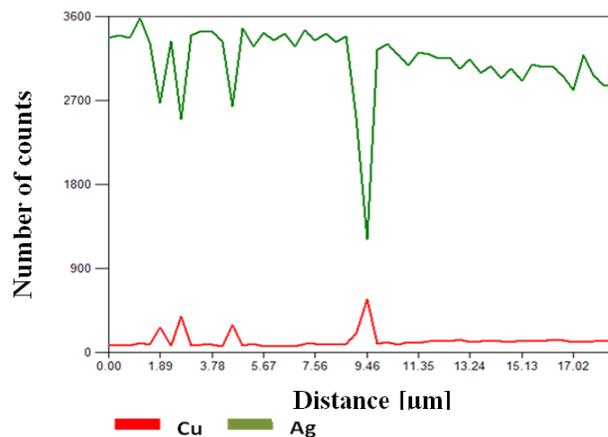


Fig. 5. Distribution of silver and copper on the cross section of the sample AgCu7 alloy

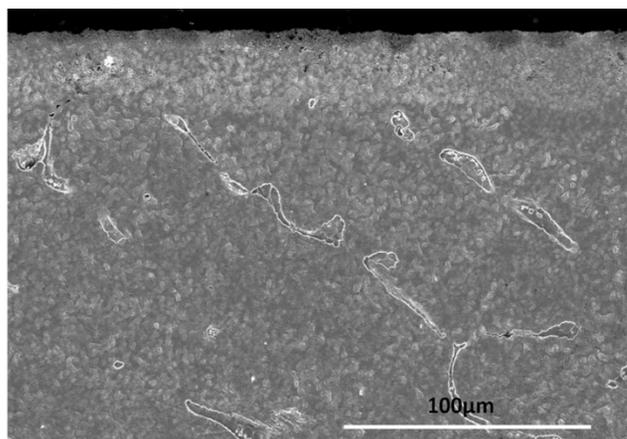


Fig. 6. The microstructure of the AgCu6Ge1 alloy, 500x

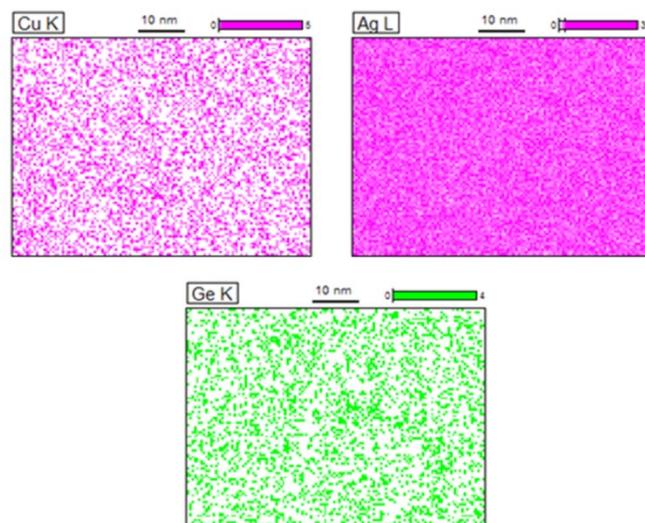


Fig. 7. The quantitative distribution of the elements Ag, Cu and Ge on the cross section of the sample

Figure 8 presents the results of hardness measurements. Gradually increasing the alloy additions, increased the hardness of the alloy.

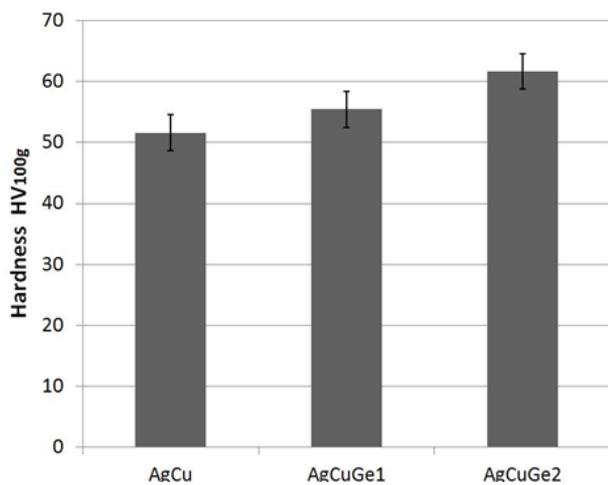


Fig. 8. The hardness of the alloys according to their composition

Figure 9 and 10 shows the dependence of the corrosion potential of the current density in the linear and logarithmic coordinates.

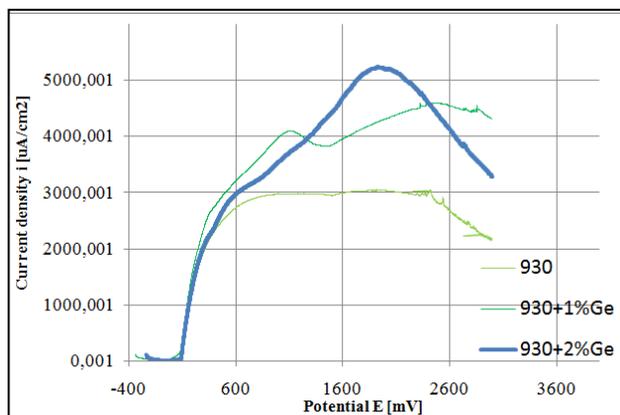


Fig. 9. Dependence of the corrosion potential of the current density in the logarithmic coordinates

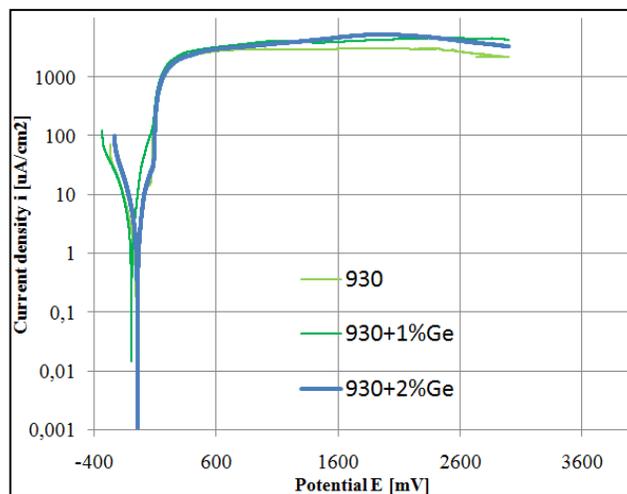


Fig. 10. Dependence of the corrosion potential of the current density in the logarithmic coordinates

Obtained polarization curves are similar, irrespective of the tested material, indicating a very similar electrochemical behavior of all the alloys in the study. This is evidenced by similar values of electrochemical parameters measured for each material, particularly corrosion current density and the value of polarization resistance and a constant current density over a wide potential range higher than the corrosion potential.

Slightly lower resistance to corrosion is characterized by an alloy containing 1% Ge - its corrosion potential is slightly lower compared to other materials, which suggests that the corrosion processes are beginning to occur slightly earlier. In addition, for the very high potentials of the anodic current density for this material increases gradually which indicates ongoing corrosion processes.

In the two other alloys current density in the range of potentials higher than 1500 mV is gradually lowered (to a greater extent for the material without the addition of germanium), suggesting formation of a stable, resistant oxide layer that protects the substrate from the medium.

Tab. 2. Parameters of corrosion process.

Silver Alloy	Corrosion potential E_{cor} [mV] pd	Corrosion Current Density I_{cor} [$\mu A/cm^2$]	Polarity resistance R_{pot} [$k\Omega cm^2$]	Anodizing Current Density for	
				$E_{anod}=1000$ mV i_{1000} [$\mu A/cm^2$]	$E_{anod}=3000$ mV i_{3000} [$\mu A/cm^2$]
AgCu	-52	0,6	13,7	2973	2167
AgCuGe1	-96	1,95	12,8	3982	4304
AgCuGe2	-47	1,8	5,3	3542	3279

5. Conclusions

Liquid metal containing dissolved alloying element-germanium, reached the eutectic at a slightly higher temperature

than AgCu alloy. Silver alloy which was used in scientific studies has a millesimal fineness of 930. Form was completely filled by the liquid metal. There has been no casting defects. During the machining of the cast has been noticed that the germanium containing alloys are less ductile and harder to be subject to rolling. On the basis of the researches it can be concluded that the obtained silver alloys containing germanium have higher hardness than the alloy containing no alloy elements. However, they are characterized by considerable fragility. Adding germanium greatly reduces the formation of the oxide layer on the surface of castings, which allows to obtain good raw castings.

Unnoticeable is a significant difference in the results of corrosion tests for the tested alloys. Sample with 1% Ge is characterized by the worst corrosion properties, while the 930 alloy is characterized as the best. However, these values are close to each other, so we can assume that all the samples reacted to the solution in a very similar way.

Analysis of obtained research allows us to notice a few trends of silver alloys with the addition of germanium. Due to the high chemical affinity for oxygen germanium alloys are more rapidly oxidized at the surface, which is confirmed by corrosion testing.

Furthermore, the zone of copper oxides is reduced, the morphology changes, which can be explained by the replacement of germanium oxide, which limits further oxidation of the alloy.

Described surface phenomena have a broader context to the products manufactured from silver alloys. They are not only jewellery and everyday items such as tableware, dishes, but also elements of technical industry, eg. electrical contacts. In both cases long term surface quality is wanted to ensure desired high surface quality test to ensure appropriate performance.

Layers of oxides and silver sulphide formed in a very short time at high temperature during casting are formed in exactly the

same way by itself at the surface of objects. Germanium addition reduces the occurrence of black copper oxide, and although they transform into the oxides are still transparent to visible radiation, which do not spoil the visual appearance of objects made from silver alloys.

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