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DESIGN OF ANTI-TARNISH STERLING SILVER Ag-Cu-Zn ALLOY AND INVESTIGATION OF SILICON ADDITION INFLUENCE ON MECHANICAL AND CORROSION CHARACTERISTICS

Article Highlights

- Design of anti-tarnish sterling silver Ag-Cu-Zn alloy is presented in the paper
- Influence of silicon addition on mechanical and corrosion characteristics was investigated
- Anti-tarnish characteristics of Ag-Cu-Zn-Si alloys were identified
- Corrosion parameters in four different solutions were determined

Abstract

This paper presents investigations of the influence of silicon addition on the mechanical and corrosion characteristics of the sterling silver Ag-Cu-Zn alloys. The procedure for obtaining Ag-Cu-Zn-Si alloys in small ranges of composition was also presented. Vickers hardness tests and three electrochemical tests were performed on the samples in this study. Open circuit potential measurements, linear polarization resistance method, and potentiodynamic polarization tests were employed to determine corrosion characteristics of the alloys. The materials were tested in 0.9% NaCl solution, artificial sweat, 0.1 and 0.01 M sodium sulfide solutions. It was shown that addition of silicone increases hardness and generally improves sulfidation resistance and corrosion characteristics in near-neutral chloride solutions of the Ag-Cu-Zn alloys.

Keywords: silver, alloy, sulfidation, Ag-Cu-Zn-Si system.

Silver is a precious metal with a white metallic luster which is in daily use and whose discovery occurred very early in history along with copper and gold and it is one of the monetary metals. It is a rare precious metal and it owes its long and continuous importance in human civilization largely to its esthetic values, its physical characteristics and durability, and then the fact that it is a rare and not very accessible metal, with confirmed important physicochemical and biomedical features. These characteristics have positioned silver as an important metal in technology, medicine and on the precious metals market. About

70% of the total world production of silver is now used in electronics, electrical engineering and medicine, while 30% is used in the jewelry industry and for the production of silver coins and everyday objects. Due to its purity, fine silver is too soft to use for everyday purposes, and it is often mixed with copper and other metals, depending on the nature of its use. Thus, metals are often added in order to make it harder. The minimum silver content in jewelry that exists in most countries, in Serbia as well, is 92.5%, that is, jewelry is marked 925 to represent the 92.5% of pure silver. The silver that meets the standards is called sterling silver and contains at least 92.5% silver and up to 7.5% copper and other metals such as nickel, zinc and the like [1].

Due to the thermodynamic stability of Ag and Cu sulfides, silver and sterling silver are subject to darkening of the metal or alloy surface, a process called tarnishing, which is of great importance in the jewelry

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and dental applications. The alloys that are sensitive to these processes include primarily alloys with high silver content and alloys with low content of gold or platinum-group metals, with or without silver in its composition [1-3]. This phenomenon is mainly linked to atmospheric corrosion, but it also occurs in corrosion in solutions, due to the influence of sweat or saliva.

The main groups of compounds that are responsible for tarnishing are those which contain sulfur, chlorine and nitrogen [2, 4]. So, tarnishing primarily refers to the formation of sulfides on the surface of silver and its alloys involving the effects of the sulfur-containing gases in the atmosphere, such as H₂S, carbonyl sulfide, CS₂, SO₂, NH₃ and the organic compounds which release sulfide ions in aqueous solutions or under various influences release gases (thioacetamide). Although the basic mechanisms of the process are known, the phenomenon is not theoretically fully understood [4-7]. In addition to the concentration of these gases, physical factors such as temperature, humidity of the air (atmosphere), and light have a great impact [5,6]. The reactions that lead to tarnishing are developed by oxidation with atmospheric oxygen, as confirmed by the studies of the tarnishing mechanism [7,8].

The first research regarding silver tarnishing and development of the silver alloys resistant to tarnishing dates back to the XIX century. Extensive research of resistance to tarnishing and mechanical properties of silver alloys was published in the 1920s [9]. Several systems of silver alloys with anti-tarnish characteristics, good mechanical properties, and possibility of processing are being patented since the last decades of the XX century [10-14]. The patented alloys are generally multicomponent systems, which often contain three to four basic alloying metals with the addition of a few more micro-alloying elements. Patents often contain dozens of the mentioned alloys, but their applicability is rarely confirmed in practice. The impact of individual elements or their combination on the mechanical properties and resistance to corrosion and tarnish are mainly studied in published works [15-18].

Silicon is an element which strongly contributes to the reduction of tarnishing and in particular the "firestain" effect due to a higher affinity to oxygen than Ag, Cu and Zn in which alloys play the role of deoxidizer of molten alloy. Si prevents dark layers of copper oxide, or "firescale" to form. It creates surface protective films on the surface (it is passivated), which contributes to reducing the tarnishing tendency. It is particularly effective with zinc as a protection against tarnishing in the system Ag-Cu-Zn [16], while as a supplement to sterling silver, its effect is only moder-

ate [17]. It also increases brittleness and hardness of silver and in larger concentrations (over 1%) does not improve resistance to tarnishing.

The aim of the investigation was to obtain series of sterling alloys, that belong to the Ag-Cu-Zn-Si system, with precisely defined chemical compositions, and to determine hardness and corrosion characteristics in chloride and sulfide media.

EXPERIMENTAL

Materials and preparation of samples

Constituent metals Ag, Cu and Zn with purity of 99.99% were produced by a recycling process. More details and analytics of the process can be found elsewhere [19]. Master alloys were: CuZn28 obtained from the pure metals and commercial CuSi10 alloy from Wieland-Werke AG, Germany (grade CuSi10(A), CM231E, EN 1981: 2003). The alloys were prepared by induction melting at a temperature of 900 °C in a graphite crucible and vacuum casting into a graphite mold preheated to 350 °C. Ingots were cylindrical with 8 mm in diameter and samples weighed 30±0.2 g. The weight loss during melting was less than 0.5%. The desired composition of alloys is given in Table 1.

Table 1. Desired chemical compositions (%) of studied alloys with 92.50% of Ag

Alloy	Cu	Zn	Si
AgCu6.5Zn1	6.50	0.00	0.00
AgCu6.4Zn1Si0.1	6.40	1.00	0.10
AgCu6.3Zn1Si0.2	6.30	1.00	0.20
AgCu6.2Zn1Si0.3	6.20	1.00	0.30

All chemicals used were of analytical grade produced by Merck (Germany). All solutions were prepared with double-distilled water with conductivity less than 1 μS/cm. A solution of artificial sweat was made according to EN 1811:1999 [20] with the following composition: sodium chloride 0.5%, lactic acid 0.1% and urea 0.1%; the pH was adjusted to 6.5.

Chemical and mechanical characterization

Silver, copper, zinc, and silicon were analyzed by AAS (Perkin Elmer 2380). The chemical compositions of the four prepared alloys are given in Table 2.

Hardness tests were performed using the HV10 test, using a 98.1 N force, with the apparatus type Kleinhärter prüfen für Vickers, Knoop, und Ritzhärte produced by LEITZ 2. The values given for the Vickers hardness are the average of the three measured values.

Table 2. Registered chemical compositions (%) of the obtained alloys

Alloy	Ag	Cu	Zn	Si	Total impurities
AgCu6.5Zn1	92.61	6.30	1.07	0.00	0.02
AgCu6.4Zn1Si0.1	92.58	6.18	1.06	0.12	0.06
AgCu6.3Zn1Si0.2	92.53	6.06	1.13	0.22	0.06
AgCu6.2Zn1Si0.3	92.57	6.02	1.04	0.34	0.03

Electrochemical characterization

Electrochemical measurements were carried out in a conventional three-electrode cell. The working electrodes were of silver alloys of composition given in Table 2, sealed in a polyacrylic resin. The working surface of these electrodes was 0.50 cm². Platinum sheet was used as the counter electrode. The potential of the working electrodes was measured relative to a saturated calomel reference electrode (SCE).

A potentiostat/galvanostat 600 Reference™ (Gamry Instruments Inc.) and software package Gamry Framework (Version 6.25) was used for the electrochemical experiments. A Gamry Echem Analyst software package for analyzing the electrochemical data was used for analysis of the results and determining the corrosion parameters.

Before each measurement, a sample was ground with a series of SiC abrasive papers and then polished using 1 μm of diamond paste. After polishing, the electrode was thoroughly washed with distilled water and degreased with absolute (99.8%) ethanol (Merck, Germany).

The experiments were carried out at temperature of 25±0.5 °C. The open circuit potential (OCP) was measured for a period of 60 min. The linear polarization resistance was measured at potentials of ±20 mV in relation to OCP at the potential rate change of 0.125 mV/s. The Tafel polarization curves were measured at the potentials of ±250 mV in relation to OCP at the potential rate change of 1.0 mV/s.

RESULTS AND DISCUSSION

Casting of the alloys, thermodynamic considerations and mechanical characterization

In order to obtain samples with identical compositions except different silicon concentrations in the range of 0 to 0.3 wt.% requires accurate control of the melting parameters and precise calculation for melting charges. The use of a master alloy is mandatory to avoid zinc evaporation which leads not just to its losses, but also to high porosity of the samples. Thus, temperature should not exceed 100 °C from the evaluated melting point of the alloys (approx. 800 °C) [21].

Silver alloys with the silver content of sterling silver (92.5%) with copper concentrations higher than 5% are usually two-phase systems. Low solid solubility of copper in silver is clearly evident from Figure 1 [22]. Consequently, cast alloy structure will normally contain a silver solid solution (Ag-rich fcc (α) phase and a Cu-rich fcc (β) phase).

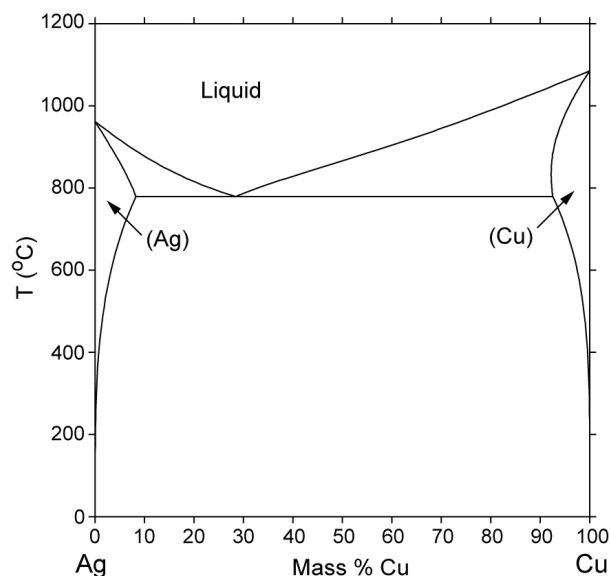


Figure 1. Ag-Cu phase diagram [22].

Silicon is poorly soluble in silver, and it is usually dissolved in the copper-rich phase in the Ag-Cu-Si system [17]. For this reason, silicon is often added to an alloy in the form of a master alloy. Subsequently, a practical way to introduce Si into a Ag-Cu-Zn system is to add Cu-Si as master alloy. In this binary system α phase is obtained for copper concentrations higher than 94.6%. However, CuSi10 was used instead of CuSi5, to allow for zinc to be introduced through the master alloy (α brass).

High zinc and silicon content, under the sterling silver compositions of Ag-Cu-Zn-Si alloys, could lead to intermetallic compounds formation because zinc promotes the formation silicide phases [21]. However, for alloys with up to 2.5% Zn and 0.2% Si the amount of intermetallic compounds remains relatively small [23]. This means that they could be considered (simplified) as two-phased alloys. Lower content of zinc allows higher concentration of Si without the formation of intermetallic compounds. The investigated alloys belong precisely to this group. These alloys are still easily mechanically processed, which is of particular importance in the jewelry industry.

In this type of alloys increasing zinc and silver content decreases hardness, and *vice versa* for copper and silicon. With near constant content of Ag, Cu

and Zn, it is expected that increasing silicon content should improve hardness. Experimental results confirmed this reasoning, as shown in Figure 2.

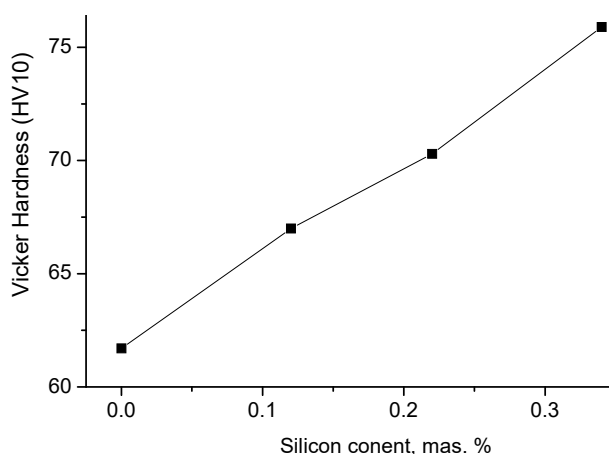


Figure 2. Influence of silicon concentration on the hardness of alloys.

The hardness of the samples is plotted as a function of increasing Si concentration in Figure 2. It is obvious that samples with higher concentration of Si have greater hardness, and that alloys with approximately 0.1 and 0.2% Si have the smallest difference in value than any two consequent samples. As can be seen in Figure 2, hardness rises almost linearly with Si concentration.

Corrosion characterization

Corrosion behavior of the Ag-Cu-Zn-Si alloys is directly related with the tarnish effect and generally

changes of color in different corrosion environments. It has been investigated in four solutions, using three methods of testing. Corrosion characteristics in the presence of sulfide are the most critical for evaluation of the resistance to tarnishing.

Parameters of corrosion in 0.01 mol/dm³ Na₂S solution

Measurement results of the open circuit potential (OCP), Tafel slopes, and coefficient *B* for determining the corrosion current from the polarization resistance measurements are shown in Table 3.

Table 3. The Tafel slopes, coefficient of the Stern-Geary equation (*B*), and the open circuit potential, 0.9% NaCl, 25 °C

Alloy	β_a mV/dec	β_k mV/dec	<i>B</i> mV	OCP, mV vs. SCE, $t = 3.6$ ks
AgCu6.5Zn1	105.4	-162.3	27.74	-129.1
AgCu6.4Zn1Si0.1	66.8	-132.9	19.31	-121.2
AgCu6.3Zn1Si0.2	73.7	-151.6	21.53	-121.0
AgCu6.2Zn1Si0.3	84.3	-111.1	20.81	-118.6

Tafel slopes are obtained from anodic and cathodic polarization curves, in the apparent Tafel region, shown in Figure 3.

Parameters from polarization measurements determined by Tafel extrapolation method are used for determination of corrosion current density (j_{corr}) by linear polarization resistance (LPR) method. Values of the polarization resistance (R_p) were determined by means of the well-known Stern-Geary equation [24]:

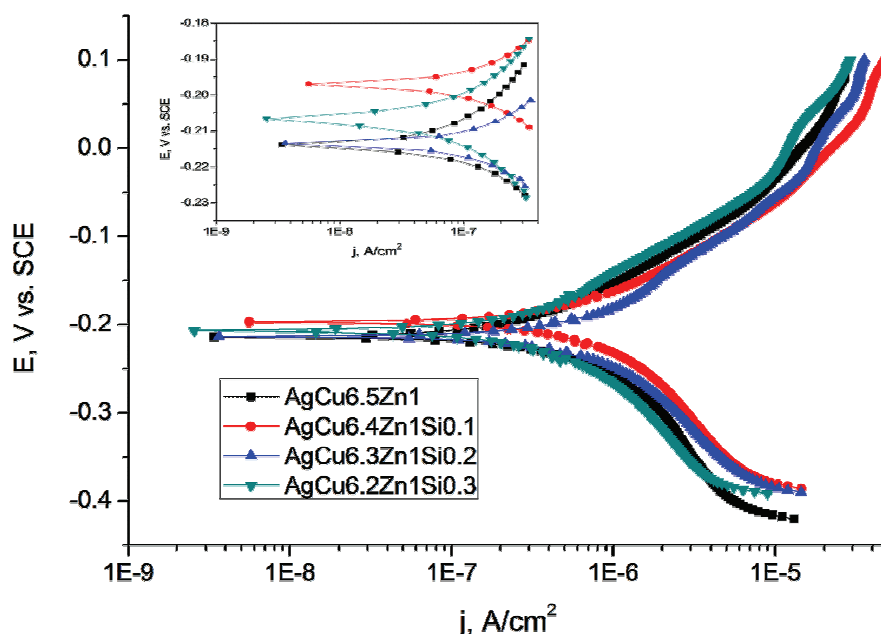


Figure 3. Potentiodynamic polarization curves for the Ag-Cu-Zn-Si alloys in 0.01 mol/dm³ Na₂S solution.

$$j_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + |\beta_c|)} \frac{1}{R_p} = \frac{B}{R_p} \quad (1)$$

where β_a and β_c are Tafel slopes for the partial anodic and cathodic processes, respectively, B is the proportionality constant, defined in the equation itself.

R_p is defined by Eq. (2):

$$R_p = \left(\frac{\Delta E}{\Delta j} \right)_{\Delta E \rightarrow 0} \quad (2)$$

Corrosion parameters obtained by both methods are given in Table 4.

Table 4. Corrosive parameters of alloys in 0.01 mol/dm³ Na₂S solution at 25 °C

Alloy	Linear polarization			Tafel	
	R_p / kΩ·cm ²	i_{corr} / nA·cm ⁻²	E_{corr} / mV vs. SCE	i_{corr} / A·cm ⁻²	E_{corr} / mV vs. SCE
AgCu6.5Zn1	38.83	879.4	-212.2	776.9	-214.0
AgCu6.4Zn1Si0.1	27.94	1100	-195.2	957.0	-197.0
AgCu6.3Zn1Si0.2	29.63	1054	-206.3	909.1	-210.0
AgCu6.2Zn1Si0.3	45.41	670.9	-201.4	557.0	-202.0

The addition of Si in low concentrations slightly increases the corrosion current, wherein the further increase in silicon concentration leads to the reduction of j_{corr} . The alloys with 0.12 and 0.22% Si have very similar values. The alloy with the highest Si has a lower j_{corr} value.

Parameters of corrosion in 0.1 mol/dm³ Na₂S solution

The measured and analyzed results with the same methods in 0.1 mol/dm³ Na₂S solution are given in Tables 5 and 6.

Table 5. The Tafel slopes, coefficient of the Stern-Geary equation (B), and the open circuit potential, 0.1 mol/dm³ Na₂S at 25 °C

Alloy	β_a mV/dec	β_k mV/dec	B mV	OCP, mV vs. SCE, $t = 3.6$ ks
AgCu6.5Zn1	102.9	-144.1	26.07	-447.9
AgCu6.4Zn1Si0.1	84.7	-127.9	22.13	-437.0
AgCu6.3Zn1Si0.2	95.0	-134.5	24.18	-439.1
AgCu6.2Zn1Si0.3	64.7	-108.3	17.59	-427.5

It can be seen from Table 6 that j_{corr} values are higher in more concentrated Na₂S solutions. The dif-

Table 6. Corrosive parameters of alloys in 0.1 mol/dm³ Na₂S solution at 25 °C

Alloy	Linear polarization			Tafel	
	R_p / kΩ·cm ²	i_{corr} / μA·cm ⁻²	E_{corr} / mV vs. SCE	i_{corr} / μA·cm ⁻²	E_{corr} / mV vs. SCE
AgCu6.5Zn1	10.65	2.448	-449.0	2.39	-443.4
AgCu6.4Zn1Si0.1	15.49	1.429	-438.4	1.49	-438.0
AgCu6.3Zn1Si0.2	14.68	1.647	-440.8	1.58	-442.5
AgCu6.2Zn1Si0.3	19.65	0.895	-429.4	0.780	-430.0

ference for the AgCu6.2Zn1Si0.3 is the smallest, but for the alloy without Si it is almost tripled. This is clear indication that Si improves corrosion and sulfidation resistance in Ag-Cu-Zn system. Increased values for the j_{corr} and more negative for the OCP (Table 6) prove that the solution with higher concentration of S²⁻ ions is more corrosive, as expected.

Parameters of corrosion in near-neutral chloride solutions

While not as critical as sulfidation, tarnish induced by chloride ions is also important for the alloys used in jewelry industry. Isotonic (0.9%) sodium chlo-

ride solution and a solution of artificial sweat (EN 1811:1999) were used for the evaluation of the Si effect on corrosion and tarnish characteristics of investigated alloys in near-neutral chloride solutions.

The results for artificial sweat, measured and analyzed with the same methods and conditions as for sulfide solutions, are given in Tables 7 and 8.

Table 7. The Tafel slopes, coefficient of the Stern-Geary equation (B), and the open circuit potential, artificial sweat at 25 °C

Alloy	β_a mV/dec	β_k mV/dec	B mV	OCP, mV vs. SCE, $t = 3.6$ ks
AgCu6.5Zn1	92.7	-61.8	16.10	-175.2
AgCu6.4Zn1Si0.1	76.1	-90.5	17.95	-108.4
AgCu6.3Zn1Si0.2	108.1	-115.8	24.28	-171.5
AgCu6.2Zn1Si0.3	89.4	-107.9	21.23	-71.34

The alloy containing 0.34% Si has the lowest corrosion current density, followed by the Si-free alloy (Table 8). It also has the most positive corrosive potential (Table 7) and indubitably is the most resistant in the artificial sweat. The addition of Si in low concen-

Table 8. Corrosive parameters of alloys in artificial sweat at 25 °C

Alloy	Linear polarization			Tafel	
	$R_p / \text{k}\Omega \cdot \text{cm}^2$	$i_{\text{corr}} / \text{nA} \cdot \text{cm}^{-2}$	$E_{\text{corr}} / \text{mV vs. SCE}$	$i_{\text{corr}} / \text{A} \cdot \text{cm}^{-2}$	$E_{\text{corr}} / \text{mV vs. SCE}$
AgCu6.5Zn1	26.14	615.9	-177.6	545.0	-180.5
AgCu6.4Zn1Si0.1	20.34	882.5	-110.1	816.0	-110.7
AgCu6.3Zn1Si0.2	29.35	827.3	-172.5	767.9	-171.0
AgCu6.2Zn1Si0.3	37.70	563.2	-72.44	453.1	-70.45

trations (up to 0.22%) slightly increases the corrosion current, wherein the increase in Si concentration (to 0.34%) leads to the reduction of j_{corr} . The alloys with 0.12 and 0.22% Si have very similar values. Increasing the corrosion current density with the small addition of silicon corresponds to the published results [17,19]. However, differences in this investigation are much lower. Furthermore, the surfaces of samples with 0.12 and 0.22% Si are bright after anodic polarization, as are the other two samples. Based on the results, the effect of silicon and its concentrations cannot be clearly observed in the alloy. A fairly good result of the Si-free alloy in comparison with the one containing Si, is particularly unexpected.

The results for the 0.9% NaCl solution, measured and analyzed with the same methods and conditions as for sulfide solutions, are given in Tables 9 and 10.

Table 9. The Tafel slopes, coefficient of the Stern-Geary equation (B), and the open circuit potential, 0.9% NaCl, 25 °C

Alloy	β_a mV/dec	β_k mV/dec	B mV	OCP, mV vs. SCE, $t = 3.6$ ks
AgCu6.5Zn1	105.4	-162.3	27.74	-129.1
AgCu6.4Zn1Si0.1	66.8	-132.9	19.31	-121.2
AgCu6.3Zn1Si0.2	73.7	-151.6	21.53	-121.0
AgCu6.2Zn1Si0.3	84.3	-111.1	20.81	-118.6

The lower corrosion current densities (Table 10) are more evident in 0.9% NaCl solution than in artificial sweat. More positive corrosion potentials (open circuit potentials) are also in favor that most of the alloys are more resistant in the NaCl solution. The effect of silicon is obvious. The addition of silicon in any concentration reduces the corrosion rate, though

it is not in compliance with some literature data [17]. The trend is similar to the results in 0.1 mol/dm³ Na₂S solution. From the parameters in Table 10 is also clear that 0.9% NaCl is the least corrosive solution of all tested.

Figure 4 shows j_{corr} for four solutions: artificial sweat, 0.9% NaCl, 0.1 M Na₂S, and 0.01 M Na₂S. The value of the corrosion current was taken as the arithmetic mean value of the LRP and Tafel method.

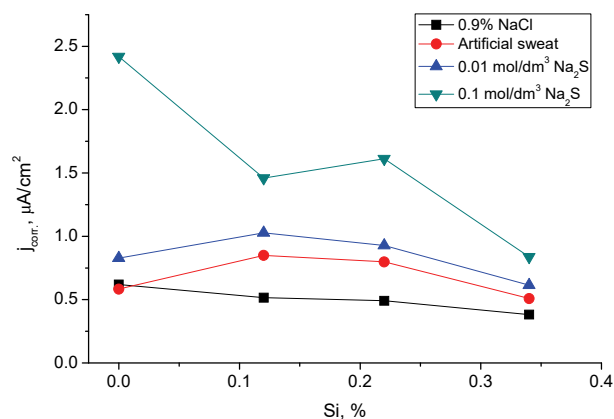


Figure 4. Values of the corrosion current densities for all four alloys in all four solutions.

From Figure 4 it can be seen that the most of the values of j_{corr} for all solutions are below 1 µA/cm², except Na₂S with concentration of 0.1 mol/dm³. The same trend of the effect of Si concentration in alloy is noticeable for solutions 0.9% NaCl and 0.1 mol/dm³ Na₂S. Corrosion current density decreased nearly linearly with concentration increase of silicon, as can be seen in Figure 4. In the two other solutions, 0.01 mol/dm³ Na₂S and artificial sweat, the influence of silicon addition differs greatly from the previous. Most

Table 10. Corrosive parameters of alloys in 0.9% NaCl solution at 25 °C

Alloy	Linear polarization			Tafel	
	$R_p / \text{k}\Omega \cdot \text{cm}^2$	$i_{\text{corr}} / \text{nA} \cdot \text{cm}^{-2}$	$E_{\text{corr}} / \text{mV vs. SCE}$	$i_{\text{corr}} / \text{A} \cdot \text{cm}^{-2}$	$E_{\text{corr}} / \text{mV vs. SCE}$
AgCu6.5Zn1	42.70	649.7	-129.6	587.5	-130.2
AgCu6.4Zn1Si0.1	35.30	547.0	-122.8	483.5	-123.7
AgCu6.3Zn1Si0.2	41.28	521.6	-120.5	460.0	-122.0
AgCu6.2Zn1Si0.3	46.84	444.3	-118.7	320.0	-120.5

obvious in Fig. 4 is the practically identical behavior of the alloys in solutions artificial sweat and 0.01 M Na₂S. The only difference was that the corrosion current density values are proportionally higher in a more corrosive solution (0.01 mol/dm³ Na₂S).

CONCLUSION

This study was carried out to investigate mechanical and corrosion characteristics of the alloys of the Ag-Cu-Zn and Ag-Cu-Zn-Si systems. It was shown that a highly controlled melting and casting process is required to obtain precise compositions. Several conclusions can be drawn from the investigation:

1. Silicon increased hardness of the casted alloys of the Ag-Cu-Zn system with 92.5 wt.% Ag. The smallest differences are between 0.12 and 0.22% of silicon content.

2. Si directly affects the reduction of j_{corr} in the 0.1 mol/dm³ Na₂S and 0.9% NaCl solutions.

3. In the 0.01 mol/dm³ Na₂S and artificial sweat only high concentration of Si (0.34%) leads to lower values for j_{corr} and smaller Si concentrations slightly increase this parameter.

4. Very similar results were obtained in all tests for the samples with 0.12 and 0.22% Si indicating that the addition of Si gives the best results, regarding lowering of the corrosion current, only with concentration above 0.3% Si. However, some improvement could be obtained with very low concentrations of Si, even lower than 0.1% Si.

5. All tested alloys have shown good tarnish resistance. It can be seen from the small j_{corr} values and the fact that none of them changed color after slow polarization to 0.25 V above OCP.

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NAUČNI RAD

DIZAJN LEGURA STERLING SREBRA Ag-Cu-Zn OTPORNIH NA TAMNENJE I ISPITIVANJE UTICAJA DODATKA SILICIJUMA NA MEHANIČKE I KOROZIVNE KARAKTERISTIKE

Ovaj rad prezentuje istraživanja uticaja dodatka silicijuma na mehaničke i korozivne karakteristike AgCuZn legura sterling srebra. Takođe je predstavljen postupak za dobijanje legura Ag-Cu-Zn-Si u malim opesezima sastava. Na uzorcima u ovoj studiji urađeno je merenje tvrdoće po Vickersu i tri metode elektrohemijskih ispitivanja; merenje potencijala otvorenog kola, metoda linearnog polarizacionog otpora i potenciodimanička polarizaciona merenja su korišćena za određivanje korozivnih karakteristika legura. Materijali su bili ispitivani u 0,9% rastvoru NaCl, veštačkom znoju, 0,1 i 0,01 M rastvorima natrijum-sulfida. Pokazano je da dodavanje silicijuma povećava tvrdoću i generalno poboljšava otpornost na sulfidaciju i korozivne karakteristike Ag-Cu-Zn legura u blisko neutralnim hloridnim rastvorima.

Ključne reči: srebro, legura, sulfidacija, Ag-Cu-Zn-Si sistem.