INFLUENCE OF ZINC ADDITION ON ANTI-TARNISH SILVER ALLOYS IN FOUR DIFFERENT SYSTEMS

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The presented paper investigates the influence of zinc addition on corrosion characteristics of different sterling silver alloy systems. Open circuit potential measurements, linear polarization resistance method, and potentiodynamic polarization tests were employed to determine the corrosion characteristics of the alloys. The materials were tested in an Artificial Sweat, 0.9% NaCl, and 0.01M Na_2S solutions. Based on the presented results, it could be concluded that zinc has the most significant direct impact. The benefits of zinc addition are especially noticeable in aluminum-containing alloy systems, but only up to 3.7 % of Zn. The best results are achieved for alloy AgCu1.9Zn3.7Al1.6Si0.3.

Keywords: atmospheric corrosion, silver, alloys, anti-tarnish; alloy

Introduction

Metal and alloy tarnishing is a corrosion process that appears as black spots on the surface of the material making it unsuitable for use not only in jewelry making but also for electrical and dental purposes. Although there are several primary causes of surface tarnishing in silver and its alloys, they can be divided into groups based on the sorts of compounds that cause tarnishing. Sulfur, chlorine, and nitrogen-containing chemicals are the dominant groups [1, 2]. Physical variables, temperature, humidity, and illumination, have a major impact in addition to the concentration of gases containing the aforementioned elements [3, 4].

The first studies on silver tarnishing and the creation of anti-tarnishing silver alloys date to the 19th century. In the 1920s substantial research on silver alloys' mechanical characteristics and tarnishing resistance was published [5]. From the late 1800s to the present, several silver alloy systems with anti-tarnish capabilities, high mechanical features, and processing potential have been patented [6–10].

The multicomponent systems, which frequently include three to four basic alloying metals with the addition of a few more micro-alloying elements, are patented alloys in general. Hundreds of the alloys mentioned above are frequently included in patents, although their practical usefulness isnt as frequently proven. Published works [11–14] focus mostly on the effects of individual components or their combinations on mechanical qualities and resistance to corrosion and tarnish.

Chrome, nickel, tantalum, and zinc were the first three components of an alloy to be examined historically. Nickel was dissolved in silver using Sb, Sn, Zn, or Cd. Sb and Cd are not acceptable as hazardous metals from today's perspective. The best results in the research at the time were for alloys based on silicon and zinc, and one of the first anti-tarnish silver alloys to be commercially accessible was Ag92.5Si4Cd3.5 and Ag93Zn6.5Na0.5 [5].

Alloys in the Ag-Cu-Zn-Si system are used for tarnish-resistant commercial alloys. A microalloying component is added for crystal grain refining. Zinc is added up to 2.5% and silicon maximally 0.2% [15]. The Cu/Zn ratio is important for tarnish resistance. A higher ratio considerably increases tarnish resistance in alloys with 94% Ag, but not that high. Ag-Cu-Zn alloy is favorable for recycling, and several production technologies have been developed.

Previous research of authors [16, 17] was focused on investigating the influence of silicon addition to standard sterling silver alloy and replacement of copper with silicon in the range from 0.05 to 0.3% [16] and additionally replacement of 1% of copper with zinc [17].

Investigations showed that increasing the silicon content decreases the j_k value in all investigated solutions in the Ag-Cu-Zn-Si system. It is especially noticeable for the sulfide solution, as well as for the maximum concentration of Si of 0.3%. The higher zinc content additionally contributes to the increase in corrosion resistance in all environments, except in the 0.9% NaCl solution.

Additional investigations by authors [18, 19] were aimed at designing new series of anti-tarnish sterling silver alloys with the addition of aluminum, i.e., the Ag-Cu-Zn-Al-Si system. Based on previous research, several limitations were set silver content was 92.5%, silicon content was 0.3%, aluminum was added in a range from of 0.9 to 3.0%, and the ratio of Zn/Cu was 2, and it was constant. Based on the achieved results, authors have concluded that the addition of aluminum in the range 0.9-3.0% to the Ag-Cu-Zn-Si system is favorable from a corrosion point of view, and the best results are achieved for the alloy with 1.6% Al. Detail description of the patented new system and production method can be found in [19].

This paper investigated the influence of zinc addition on the corrosion resistance of all sterling silver systems authors have previously researched.

Materials and methods

Detailed descriptions of used raw materials and master alloys could be found in the previous work of authors [16-19]. Smelting of final alloys was performed in an induction furnace at a temperature of 980 °C. The process began by charging silver and then other metals and/or master alloys. Before casting graphite, molds were preheated to 250-350°C. Alloys were cast under a vacuum. For comparison reasons, an alloy of classic sterling silver (92.5% Ag and 7.5% Cu) was also cast. Designed alloy compositions are presented in Table 1.

Table 1 Designed compositions of anti-tarnish silver alloys (in wt. %).

Alloy	Cu	Zn	Si	Al	P	Ag
Ag Cu7.5	7.5					bal
Ag93 Cu6.5 Zn0.5*	6.5	0.5				bal
Ag Cu6.5 Zn1	6.5	1				bal
Ag Cu6.4 Zn1 Si0.1	6.4	1	0.1			bal
Ag Cu6.3 Zn1 Si0.2	6.3	1	0.2			bal
Ag Cu6.2 Zn1 Si0.3	6.2	1	0.3			bal
Ag Cu2.4 Zn4.8 Si0.3	2.4	4.8	0.3			bal
Ag Cu1.4 Zn2.8 Al3 Si0.3	1.4	2.8	0.3	3		bal
Ag Cu1.6 Zn3.3 Al2.3 Si0.3	1.6	3.3	0.3	2.6		bal
Ag Cu1.9 Zn3.7 Al1.6 Si0.3	1.9	3.7	0.3	1.6		bal
Ag Cu1.9 Zn3.7 Al1.6 Si0.3 P**	1.9	3.7	0.3	1.6	0.05	bal
Ag Cu2.1 Zn4.2 Al0.9 Si0.3	2.1	4.2	0.3	0.9		bal
Ag Zn4.2 Al3 Si0.3		4.2	0.3			bal

*Mechanically processed commercial alloy; **P added through master alloy during smelting

The degree of surface tanning is the value of the corrosion current density (j_{corr}). These two parameters are directly dependent: the lower j_{corr} indicates a less tanned surface. The density of the corrosion current was determined by the method of linear polarization resistance.

Electrochemical measurements were performed in a conventional three-electrode cylindrical glass cell. The working electrode was made out of investigated silver alloys and an alloy of sterling silver, embedded in polyacrylic resin. For electrochemical experiments Gamry Reference 600 potentiostat/galvanostat/ZRA was used, and for analysis of the electrochemical data and determining the corrosion parameters, a Gamry Echem Analyst software package was used.

The potential was measured concerning a saturated calomel reference electrode (SCE). The contra electrode was the platinum sheet with an area of 2 cm^2. Before each measurement, a sample was ground and then polished to a mirror finish with 0.3 μm alumina powder. After polishing, the electrode was thoroughly washed with distilled water and degreased with absolute ethanol (p.a.). The experiments were performed at a temperature of 25±1 °C. The open circuit potential (OCP) was measured for 3600 s. The linear polarization resistance (LRP) was measured at ±20 mV from the OCP with a potential rate change of 0.167 mV/s. The Tafel polarization curves were measured at the potentials of ±200 mV about OCP at the potential change rate of 1 mV/s. Tafel's method [20] was used to determine the coefficient from the Stern-Geary equation. The operating solutions were: Artifical Sweat, 0.9 % NaCl and 0.01M Na_2S.

Results and discussion

When comparing the results of all tested alloys in three solutions (artificial sweat, 0.9% NaCl solution, and 0.01 M Na_2S), the basic trends of the influence of all alloying elements can be observed, as presented in Figure 1. The most noticeable is that classic sterling silver, as a purely two-component alloy with a content of 92.5% Ag and 7.5% Cu, has a very high value of j_{corr} in the sulfide solution and, accordingly, a low resistance to sulfidization, which is generally known, but in a presented comparative view it is significantly expressed.

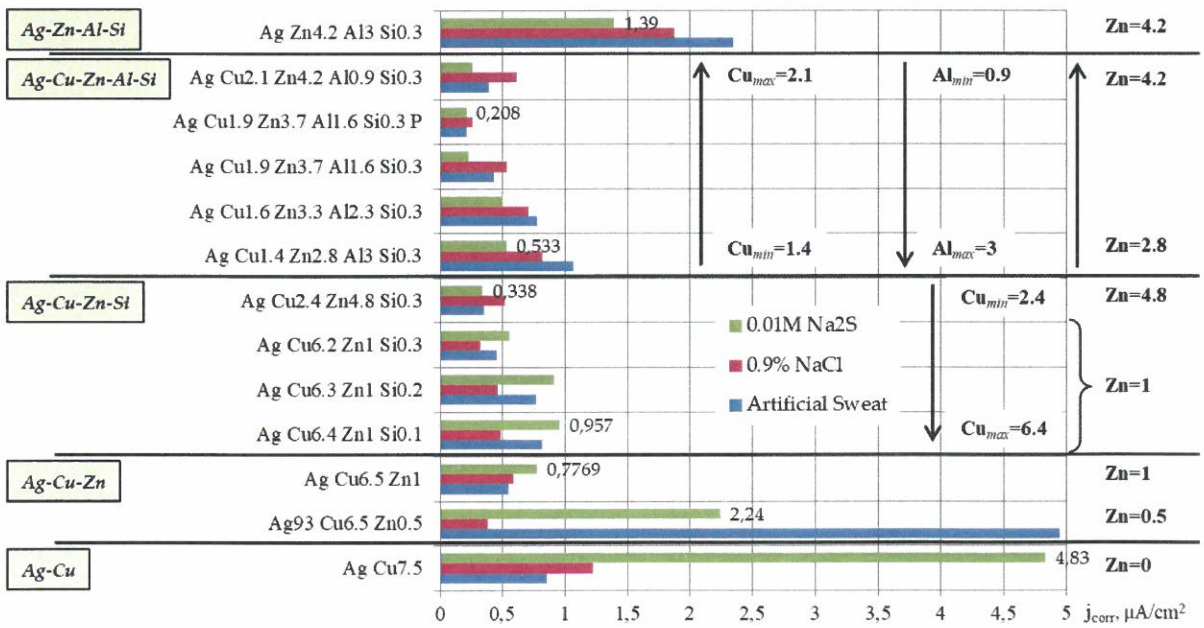

Figure 1 Comparison of corrosion current density for different anti-tarnish silver alloy systems

A small addition of zinc (0.5%) with a higher content of silver (93%) significantly reduces corrosion currents in 0.9% NaCl solution and 0.01 M Na_2S solution, while increasing in artificial sweat solution. However, the Ag93Cu6.5Zn0.5 alloy was the only one that was not tested as cast but after mechanical processing (in sheet form) because it is a commercial alloy.

The result of artificial sweat could be due to possible mechanical influences during the straightening of the sheet.

The investigation presented in Figure 1. shows that out of all the alloying elements, zinc has the greatest direct influence. It acts synergistically with Si and Al. It especially improves corrosion resistance if it is in a higher concentration than copper.

In Figure 1, it can be seen that zinc significantly affects the reduction of j_{corr} already at low concentrations (0.5% and especially 1%), when added to sterling silver without silicon. Along with silicon, higher concentrations of Zn and lower concentrations of copper increase corrosion resistance in all investigated solutions. The decrease of Cu concentration and the increase of Zn in sulfide solutions have an additional positive effect if the alloy contains Si, whereby higher concentrations have a more substantial effect.

In the Ag-Cu-Zn-Al-Si system, the increase in zinc content contributes to the decrease of j_{corr}, but only up to a value of 3.7%. A higher concentration (4.2%) increases j_{corr}, although the values are only slightly higher (good corrosion resistance is maintained). The influence is not direct because, at the same time, as the concentration of Zn increases, the content of Al decreases, so the minimum of corrosion currents is expected for values of Zn and Al that are not at the investigated range borders. Increasing copper concentration can be associated with a decrease in j_{corr}. However, that influence is indirect and low because even at 2.1% Cu, the content of the copper-rich phase is small [11], which is more important than the copper concentration itself.

An alloy with high Al and Zn content and no copper (AgZn4.2Al3Si0.3) has mean j_{corr} values that are higher than the Ag-Cu-Zn-Si and Ag-Cu-Zn-Al-Si systems and lower than sterling silver and comparable to the Ag-Cu-Zn and Ag-Cu-Si systems. This alloy has similar corrosion current density values with the AgCu7.2Si0.3 alloy. The slightly higher value in 0.01M Na_2S solution is not something expected, nor is the lower one in chloride solutions. This indicates that the absence of a copper-rich phase with Si has a positive effect on the resistance in chloride solutions. Both alloys compared have significantly better resistance in sulfide solutions than sterling silver (Ag-Cu system). Good reflection results for AgCuSi with 0.3% Si indicate that AgZn4.2Al3Si0.3 could also have excellent results according to this criterion, which is as important as the corrosion current density values.

Conclusion

Presented research shows that with the addition of alloying elements, the corrosion resistance of clastic sterling silver alloy significantly improves. Based on the presented results, it could be concluded that zinc has the most significant direct impact on the corrosion resistance. Generally, for all investigated alloys, the best corrosion characteristics are achieved in systems that contain aluminum. The benefits of zinc addition are especially noticeable in aluminum-containing alloy systems, but only up to 3.7 % of Zn. Within this system ratio of Zn/Cu was kept constant at 2, so the decrease of copper in alloy composition enhances the positive effects of zinc addition. The best results are achieved for alloy AgCu1.9Zn3.7Al1.6Si0.3. Following this, future research will provide a detailed investigation of present microstructures with an in depth explanation of the anti-tarnish mechanisms.

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