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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Selective Electrochemical Dissolution of Silver Coatings on Copper and Its Alloys

O. Bersirova[a], G. Tsesiulis[b], and V. Kublanovskii[a]

[a]*Vernadskii Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine*
[b]*Vilnius University, Vilnius, Lithuania*

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Abstract—Thiocyanate electrolyte and a mode for selective dissolution of silver coatings from reject articles made of copper alloys were suggested. The possibility of using the electrodeposited silver, obtained on the cathode in silver stripping baths, as an anode material in fabrication of silver coatings was examined.

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In the practice of silver plating, it frequently becomes necessary to remove silver coatings from reject articles and to recover silver from spent electrolytes [1]. For example, it is known that poor-quality silver coatings are removed by their electrochemical dissolution in a silver plating electrolyte or in a solution containing 50–70 g l^{-1} of KCN at 15–35°C and j_a = 0.3–0.5 A dm^{-2}. As cathodes serve carbon, graphite, or steel (12Kh18N9T) plates. Plates of the last type are allowed to be used as anodes in silver plating baths [2, 3].

There exist a number of methods for chemical removal of coatings and direct recovery of silver. For example, silver is removed from articles made of copper and its alloys in a solution containing four to nine volume parts of H_2SO_4 and one part of HNO_3. The solution temperature is 20–100°C, and the keeping time depends on the thickness of the silver coating. Articles are charged in the dry state, without trace amounts of water and oils (to preclude overetching) at a charge density of up to 25 dm^2 l^{-1}. After the removal of silver, the articles are washed in H_2SO_4, water, and running water. When the concentration of silver ions exceeds the solubility product of Ag_2SO_4, the solid phase of silver sulfate precipitates, water is added to the solution until complete dissolution of the precipitate, and then a NaCl solution, until complete precipitation of AgCl. The resulting AgCl can be used both for preparing AgSCN to be used in silver plating and for direct recovery of silver.

To obtain silver thiocyanate (AgSCN), a thoroughly washed AgCl precipitate is dissolved in a concentrated (500 g l^{-1}) KSCN solution to a concentration of 150 g l^{-1}. On preparing the solution, it is 10-fold (residual silver concentration 0.65 g l^{-1}) or 20-fold (residual silver concentration 0.085 g l–1) diluted with distilled water. The resulting precipitate of silver thiocyanate AgSCN is decanted and washed with water.

Silver can be directly recovered by fusing dried AgCl with sodium carbonate. The reaction is performed at 1100°C. This procedure yields silver ingots with a purity of no less than 99.9%

Metallic silver of the same purity can also be obtained electrochemically. The cathodic deposition of silver after a chemical dissolution of coatings is performed by its electrodeposition on a cathode made of preliminarily silver-plated stainless steel in a bath with insoluble anodes in an electrolyte of composition (g l^{-1}): AgSCN (in terms of the metal) 30–80, KSCN 300–400, Na_3PO_4 100–300, KOH 60–100; at pH 13.5–2.0 and temperature of 8–30°C.

Because the methods listed above (high-cyanate bath, mixture of highly concentrated acids, etc.) are

ecologically unsafe, the problem of silver removal from reject articles made of copper and copper alloys remains unsolved. In our opinion, the electrochemical method for silver recovery is ecologically safer, because nontoxic and noncorrosive reagents are used. In addition, this method yields almost no overetching of the copper base. The method is based on the simultaneous anodic dissolution of a silver coating and cathodic reduction of silver complexes to the metal.

For the purposes specified, the electrolyte used should provide an active dissolution of silver and a substantial polarization of the anodic dissolution of the base. The latter is achieved by the base passivation in the given electrolyte. In addition, obtaining a dense cathode deposit requires that silver complexes should be present in the electrolyte.

The aim of this study was to examine the electrochemical dissolution of a silver coating from articles made of copper and its alloys and the possibility of further use of the base without additional processing. Use of silver electrodeposited on the cathode as an anode material for obtaining refined silver or silver compounds suitable for bath adjustment is also of considerable interest.

EXPERIMENTAL

A thiocyanate electrolyte containing 300 g l^{-1} of potassium thiocyanate and 20–30 g l^{-1} of silver (in the form of AgSCN or $AgNO_3$) was chosen as the base electrolyte. This electrolyte enables use of high anode current densities, up to 8 A dm^{-2} at a current efficiency close to 100%, at a cathode current density of 1.0–1.5 A dm^{-2}, with high-quality silver coatings deposited with thicknesses of up to 100 μm (about 10 g dm^{-2}). In addition, the thiocyanate electrolyte is nontoxic.

We carried out voltammetric studies of the dissolution process with a PI-50-1 potentiostat with a PR-8 programming unit on silver samples and samples of substrate materials: copper, brass, and German silver. A saturated silver chloride electrode was used as reference. All the potentials presented here are recalculated to the hydrogen scale.

An anodic polarization curve measured on silver is shown in Fig. 1. It can be seen that active dissolution of silver is observed at potentials of +0.1 to +0.3 V. In this range of potentials, base components should not actively dissolve. As demonstrated by the results of a study of the copper dissolution in thiocyanate solutions, copper rapidly dissolves at KSCN concentrations exceeding 500 g l^{-1}. As demonstrated by inversion voltammetry (Fig. 2), only anodic formation of a difficultly soluble CuSCN film occurs at lower KSCN concentrations. The area of the anodic formation of the film somewhat exceeds that of the cathodic reduction of CuSCN to Cu, which can be attributed to chemical dissolution of the CuSCN film to give thiocyanate complexes of copper. However, the small amounts of copper passing into solution do not noticeably affect the cathodic process of silver electrodeposition, because the potentials of silver and copper deposition in thiocyanate electrolytes duffer by 0.3–0.4 V.

In the range of silver dissolution potentials, there must not occur any active dissolution of base components from copper alloys (copper, zinc, nickel) and of alloys (brass,

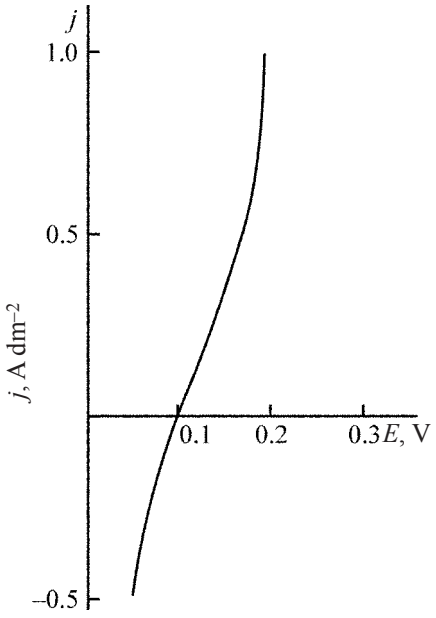

Fig. 1. Polarization curve of silver oxidation. (*E*) Potential and (*j*) current density; the same for Figs. 2–5. Concentration (g l^{-1}): $AgNO_3$ 30 (in terms of Ag) and KSCN 300.

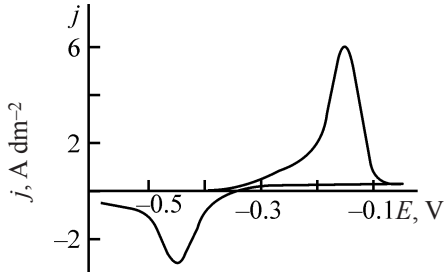

Fig. 2. Cyclic voltammetric curve of copper. KSCN concentration 300 g l^{-1}.

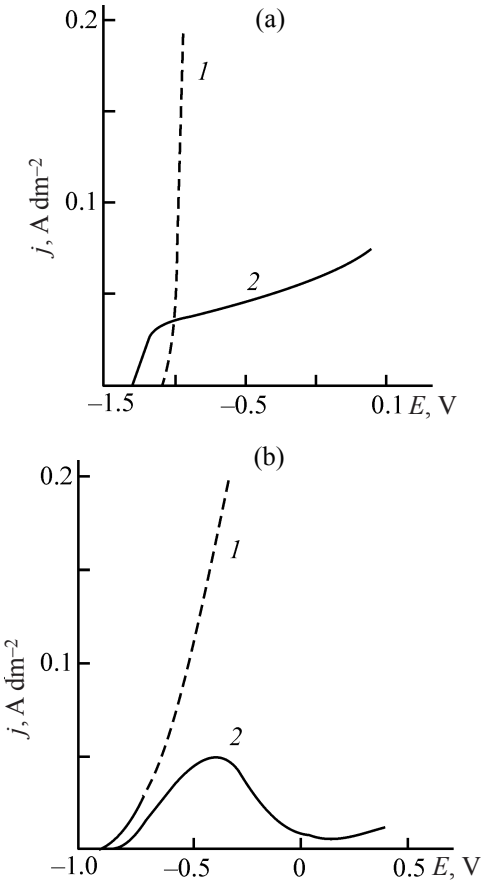

Fig. 3. Anodic polarization curves of (a) zinc and (b) brass in thiocyanate electrolytes. Na_3PO_4 concentration (g l^{-1}): (*1*) 0 and (*2*) 70; the same for Figs. 3, 4.

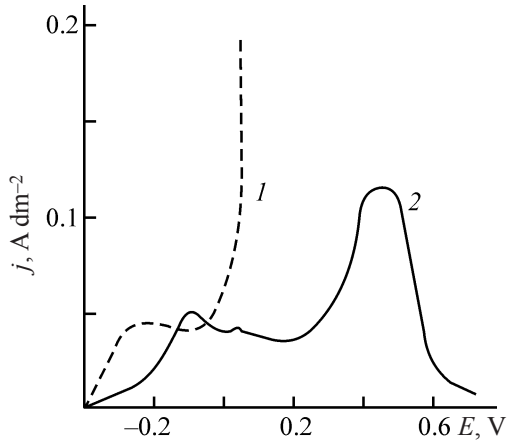

Fig. 4. Anodic polarization curves of nickel in thiocyanate electrolytes.

German silver). As, however, follows from the data in Figs. 3–6 (curves *1*), active dissolution of nickel, zinc, brass, and MNTs alloy occurs in a thiocyanate electrolyte without additives. For example, the current density of the

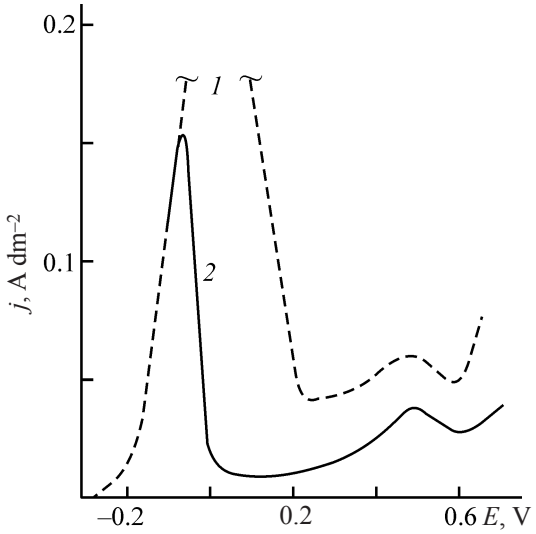

Fig. 5. Anodic polarization curves of MNTs in thiocyanate electrolytes.

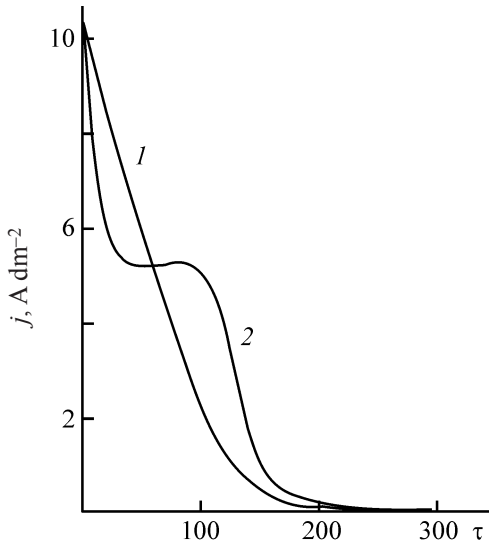

Fig. 6. Variation of the rate j_a of the anodic dissolution of silver from a planar copper surface under different conditions. (*1*) Anode potential $E = 0.2$ V; (*2*) bath voltage 0.5 V. Electrolyte composition (g l^{-1}): AgM 30, KSCN 300, and Na_3PO_4 70.

anodic dissolution of zinc at $E = 0.1$ V is 27 A dm^{-2}, and that of brass at the same potential, 12 A dm^{-2}. As a result, the base surface becomes black after the removal of the silver coating. Further use of the base requires its treatment by scratch-brushing and polishing and purification of the electrolyte to remove the anodic slime. To preclude these phenomena, it is suggested to introduce sodium or potassium triphosphates in a concentration of 70–100 g l^{-1}

into the electrolyte as a passivating agent. As can be seen in Figs. 3–5 (curves *2*), the phosphate ions introduced for this purpose diminish the rate of the active dissolution of zinc and, to a greater extent, that of brass.

It follows from the experimental data that silver coatings should be removed at potentials of +0.2 to +0.3 V. This is achieved by performing the process at a controlled bath voltage of 0.5 V. This mode of coating removal has an advantage over the process with a controlled anode potential, in which the main amount of silver dissolves at a constant current, with a sharp decrease in the current observed at the end of the process (Fig. 6, curve *2*), and this facilitates controlling the process. At the same time, a gradual decrease in the dissolution current is observed at a controlled potential (Fig. 6, curve *1*) during the entire process, which facilitates determining the end of the process.

As can be seen in Fig.6, the silver dissolution current density reaches values of 5–6 A dm^{-2} at a bath voltage of 0.5 V. To balance the anodic and cathodic processes (for a dense silver deposit to be formed at the cathode, i.e., so that the cathode current density should not exceed 1.0–1.5 A dm^{-2}), it is necessary to choose a certain ratio between the cathode and anode areas, specifically (5–7) : 1.

CONCLUSION

(1) An electrochemical method for silver removal from reject articles made of copper and its alloys was developed. For this purpose, and electrolyte of the following composition was suggested (g l^{-1}): potassium thiocyanate 300, silver nitride 23, and trisodium phosphate 70. The anode current density of silver dissolution is 5–6 A dm^{-2}, and the cathode current density should not exceed 0.8–1.0 A dm^{-2}.

(2) It is recommended to perform the electrolysis at a controlled bath voltage of 0.5–0.7 V.

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