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Electroplating of silver onto aluminum and its alloys

In this paper the structural characteristics of silver coatings electrodeposited as final coatings onto aluminum were shown. The copper coating was electrodeposited as a basic coating directly onto aluminum. Afterward, nickel and copper coatings from acidic bath were deposited. Silver was electrodeposited on the acidic bath copper coating. Also the influence of fluorides in the solution for direct electrodeposition of basic copper coating on the structure of the final silver coatings was investigated. Structural characteristics of basic copper coatings and final silver coatings were examined with scanning electron microscopy (SEM). Silver coatings can be succesfully electrodeposited as a final coating onto aluminum with nickel and copper intercoatings.

Key words: *electroplating of silver, chemical preparation, final coating, scanning electron microscopy (SEM)*

INTRODUCTION

As a construction material aluminum is becoming more and more intereseting because of its own specific characteristics: small specific mass in relation to other metals, large electrical conductivity, mechanical characteristic etc. The corrosion resistance of aluminum is very good in atmospheric conditions and in very narrow area of pH value (pH = 4-8) [1, 2]. Because of its specific characteristics and industry demands (electronic, fixed, automobile, aircraft industry, space investigations, etc.), aluminum itself presents the metal of the present and future.

In the world very much is done in the area of improving the characteristics of aluminum with alloying and surface protection processes. Improvement of the aluminum characteristics is spreading into the area of its appliance. One of the ways of surface protection are metal coatings which, although only several micrometers thick, give the base metal the properties of the metal of that coating.

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Because of the great affinity of aluminum towards oxygen and always present passive oxide film, the protection of aluminum surface is greatly hindered. In order to protect the aluminum surface, it is neccessary to chemically remove passive oxide film and to activate the surface. In the world up-to date two processes of activation of aluminum surface are worked out: a) zinc process and b) tin process. Afterwords, the other metal coatings are deposited onto activated aluminum surface (on chemical coating of zinc or tin coating) e.g. nickel, copper, silver. The process of activating aluminum surface consists of more separate phases, and it is very complicated. In order for aluminum to have wide area of application it is necessary to simplify the technology of its protection with direct electrodeposition of metal coatings on its surface.

The aim of this paper was to give contribute, also using some experimental experience in this branch through experimental work, in finding some electrolytes and optimum conditions for electroplating of final silver coatings. Besides, the chemical deposition of zinc and tin has been avoided since the copper coating was directly electroplated onto aluminum. Afterwords, nickel and silver coatings were depositred on this copper coating from the commercial baths.

EXPERIMENTAL

The experiments were performed in 1 dm^3 electrochemical cell, in pilot plant 70 dm^3 baths and in side baths 5 dm^3 in volume. The aluminum samples (5 cm x 5 cm) of technical quality were used. The solutions were prepared from p. a. chemicals and demineralized water.

The following operations were done in pilot plant scale: degreasing, pickling I, pickling II, nickel electrodeposition, copper electrodeposition from acidic bath and silver electrodeposition.

The base copper coating was deposited onto aluminum from electrochemical cell from the solution 5 (I, II, III). The side baths were used in the process of bright dipping.

The solutions contents used and work conditions in the experiments were as follows:

1. Degrease solution [3]:

   50% Na_2CO_3 + 50% $Na_3PO_4 \times 10H_2O$; (5% aqueous solution), t = 60 – 70^0 C; τ =15 min; pH = 7,5.

2. Solution I for pickling [3]:

   20% NaOH + 2% NaF; t = 70-75^{0}C; τ = 2-5 min

3. Solution II for pickling [3]:

   HNO_3 (550 cm^3/dm^3) + H_2SO_4 (200 cm^3/dm^3) + NaF (140 g/dm^3); room temperature; τ =5 min

4. Bright dipping solution [3]:

   HNO_3 (20%) + HF (10%); room temperature; τ =5 min

5. Solutions for copper electrodeposition:

   Solution I [4]:

   $CuSO_4$ (55 g/dm^3) + CH_2NH_2-CH_2OH (100 g/dm^3) + $(NH_4)_2SO_4$ (30 g/dm^3) + $Na_2SO_4 \times 10H_2O$ (75g/dm^3) + Na_2CO_3 (3 g/dm^3); room temperature; j = 0.3 A/dm^2; pH = 10.3

   Solution II [5]:

   CuCN (40 g/dm^3) + NaCN (50 g/dm^3) + free CN (4 g/dm^3) + Na_2CO_3 (30 g/dm^3) + $KNaC_4H_4O_6$ (60 g/dm^3); pH = 10.2-10.5; t = 30-35^{0}C; sample to be put under current, j = 2 A/dm^2 for the first 60 s, after 60 s j = 1 A/dm^2 and τ =10 min.

   Solution III [5]:

   $Cu(CH_3COO)_2$ (20 g/dm^3) + KCN (20 g/dm^3) + Na_2CO_3 (20 g/dm^3); j = 0.5 A/dm^2; τ = 3-5 min, sample to be put under current.

6. Bath for nickel electrodeposition [3]:

   $NiSO_4 \times 6H_2O$ (300 g/dm^3) + $NiCl_2 \times 6H_2O$ (45 g/dm^3) + H_3BO_3 (g/dm^3); j = 2 A/dm^2; τ = 45 - 50^0 C + specific agents for nickel electroplating.

7. Acidic bath for copper electrodeposition [3]:

   $CuSO_4 \times 5H_2O$ (210 g/dm^3) + H_2SO_4 (75 g/dm^3); room temperature; j = 1 A/dm^2.

8. Bath for silver electrodeposition [3]:

   Ag(met.) (20-33 g/dm^3) + KCN(free) (30-45 g/dm^3) + K_2CO_3 (30-90 g/dm^3); room temperature; j=0.3-0.5 A/dm^2; specific agents for a fully bright electrodeposit and ductility of coatings. The electrolyte should be cirulated or the work rod moves backwards and forwards.

The chemical preparation of all aluminum samples were performed in the same way in the solutions (1 - 4): chemical degreasing (15 min), pickling I (5 min), pickling II (5 min), bright dipping (5 min). Between these operations the samples were rinsed. Rinsing must at all times be thorough since the slightest trace of carry-over may at best inhibit treatment in the next bath and at worst ruin the following solution.

The morphology of the deposits (basic copper coating and final silver coating) was investigated by means of scanning electron microscopy (using a JOEL T20 microscope).

RESULTS AND DISCUSSION

Solution 5(I) gave copper coating with an excellent adhesion, but solutions 5(II) and 5(III) did not give copper coating with good adhesion on aluminum; therefore the solution 5(I) is used in further examinations.

It can be seen in Fig. 1 (a-d) structural characteristics of copper coatings directly electrodeposited from solution 5(I) on chemically treated aluminum surface. SEM photomicrograph of copper coating surface which was deposited from solution 5(I) without fluorides is presented in Fig. 1a. In Fig. 1 (b-d) SEM photomicrographs of copper coatings from solution 5(I) with added NaF: b) 1 g/dm^3, c) 2 g/dm^3 and d) 2.5 g/dm^3 are presented. Copper coatings were deposited τ = 40 min with current density j = 0.6 A/dm^2.

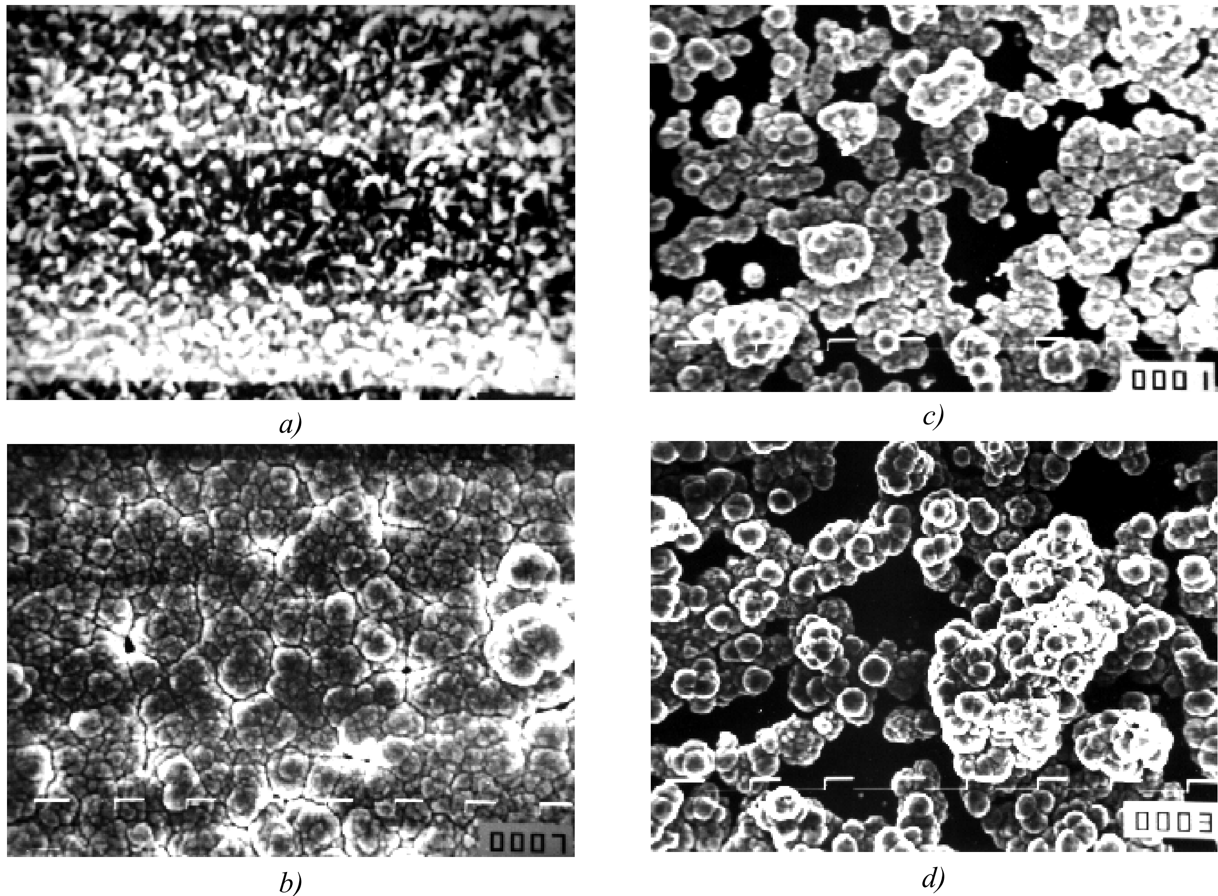


Fig 1. SEM photomicrographs of the copper coating structure deposited from the solution 5(I), τ = 40 min, at current density j = 0.6 A/dm^2 and pH = 10.3.: a) without NaF, b) with addition of 1 g/dm^3 NaF, c) with addition of 2 g/dm^3 NaF and d) with addition of 2.5 g/dm^3 NaF. Magnification x1500

Copper coating surfaces deposited from solution 5(I), with current density j = 0.6 A/dm^2, pH = 10.3 and time of deposition τ = 40 min have roughness structure, the coverage of the base metal is complete and crystalinic grains are of on uniform average size (Fig. 1a).

With addition of 1 g/dm^3 the surface of the base metal is not completely covered (some holes in beetween the coating crystals are visible), grains are bigger, the coating is more porous on the grain edge, and the formation of the new crystal layer of the coating is visible (Fig. 1b). With greater concentrations of NaF the coverage of basic metal is smaller, but the formation of new coating layers on already formed crystalizing centers is more intense (Fig. 1c and 1d).

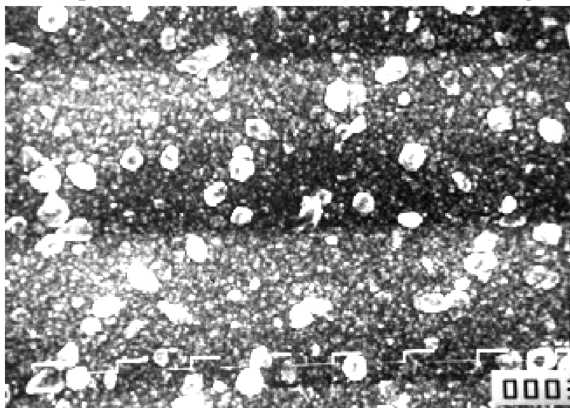
The nickel coatings were deposited, from the solution 6, on the copper coatings, from solution 5(I) (Fig. 1), at current density 2 A/dm^2 and τ = 20 min. Afterwords, copper was deposited from the acidic bath 7, at j = 1 A/dm^2 and τ = 15 min. In the end silver was electrodeposited on the acidic bath copper coating from the bath 8, at current density j = 0.3 A/dm^2 and τ = 20 min.

Fig. 2 (a-d) show SEM photomicrographs of the silver coating surfaces deposited from the bath 8. Before the silver deposited, copper coatings were deposited from the solution 5(I) on the chemically treated aluminum surface: a) without NaF, b) 1 g/dm^3 NaF, c) 2 g/dm^3 and d) 2.5 g/dm^3. Afterwords, nickel was deposited from the bath 6, and copper from bath 7. Figures are done at the same magnification of x1500 as in the previous case.

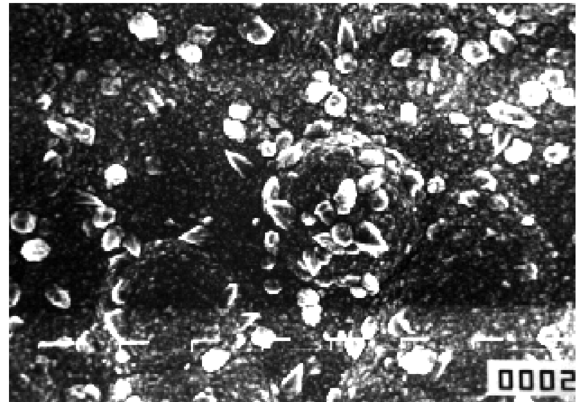
It can be seen from the Fig. 2a and 2b that the silver coatings are small grained in structure, and the minor porosity of the coating is visible. With increasing the NaF concentration in solution 5(I) the coarse-grained structure of the silver coating was obtained. That fact is confirmed with Fig. 2c and 2d where the increasing concentration of NaF gives the coarse-grained coating surface and leads to more intensive formation of new layers. This has for a consenquence the greater porosity and inhomogenity of the coating. The adhesion of the coatings was very good.

Figure 3 shows SEM photomicrographs of the silver coating surface deposited from the bath 8,

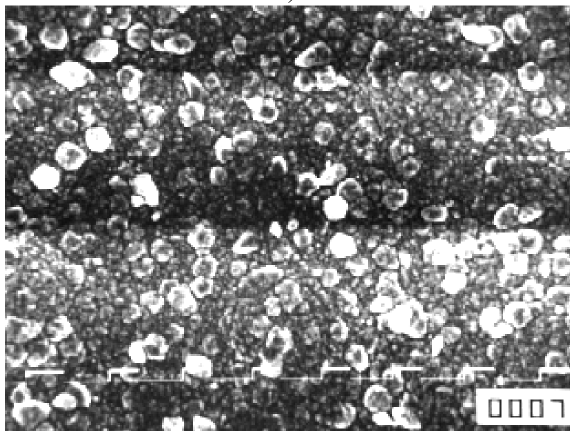
τ = 20 min. Before every silver coating on the chemically prepared surface, the copper coatings were deposited from the solution 5(I), with 1 g/dm^3 NaF at j = 0.6 A/dm^2 and τ = 40 min, and the copper coating from the bath 7, τ = 15 min.



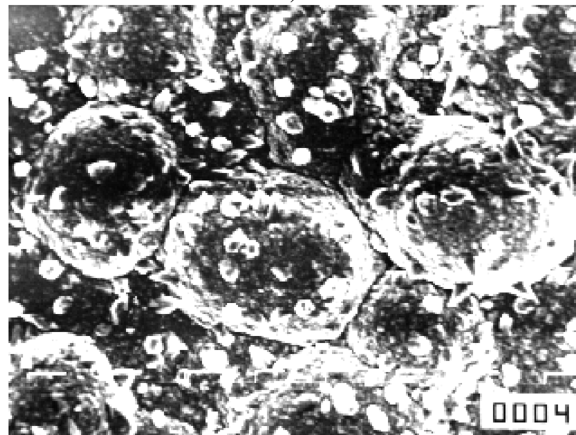
a)



c)



b)



d)

Fig 2. SEM photomicrographs of the silver coating structures deposited from the bath 8. Before the silver coating, the copper coatings were deposited from the solution 5(I): a) without NaF, b) with addition of 1 g/dm^3 NaF, c) with addition of 2 g/dm^3 NaF and d) with addition of 2.5 g/dm^3 NaF; nickel coating from the bath 6 and copper coating from the bath 7. Magnification x1500.

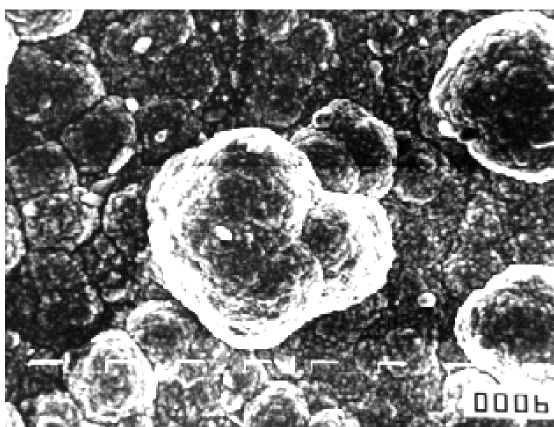


Fig 3. SEM photomicrographs of the silver coating surface deposited from the bath 8. Before the silver coating, the copper coating was deposited from the solution 5(I) with addition of 1 g/dm^3 NaF and copper coating from the bath 7. Magnification x1500.

Comparing the Fig. 3 with Fig. 2 (a-d), it can be seen that the most intense growth of the new layers, as well as the greatest porosity and roughness of the final silver coating is on the Fig. 3. Therefore it is obvious that the nickel intercoating, from the bath 6, plays very important role and has a great influence on the structure of final silver coating.

CONCLUSIONS

The aim of this paper was to give contribute, also using some experimental experience in this branch through experimental work, in finding some electrolytes and optimum conditions for electroplating of final silver coatings. Besides, the chemical deposition of zinc and tin has been avoided since the copper coating was directly elec-

troplated onto aluminum. Afterwards nickel and silver coatings were deposited on this copper coating from the commercial baths.

Results of analysis show that metallic coatings with very good structural characteristics can get beside classical zinc procedure and at direct electrochemical deposition of metallic coatings on aluminum, at exact defined conditions: concentration of plating bath, electrochemical and technological parameters.

Silver coatings can be electrodeposited onto aluminum without previous special preparation of its surface (zinc and/or tin process). Very quality silver coatings with very good adhesion were obtained when on the chemically treated aluminum, copper was electrodeposited from the solution 5(I), then nickel coating from bath 6, copper from bath 7 and silver from bath 8. The structure of the final silver coatings depends of a basic copper coating structure i.e. the concentration of NaF in the solution 5(I). It can be concluded that the silver coating follows the structure of the basic copper coating and that the intercoating of the nickel plays very important role on the silver coating structure.

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REZIME

ELEKTROHEMIJSKO TALOŽENJE PREVLAKA SREBRA
NA ALUMINIJUM I NJEGOVE LEGURE

U ovom radu su prikazani morfologija i strukturne karakteristike elektrohemijski istaloženih prevlaka srebra, kao završnih prevlaka, na aluminiju i njegovim legurama. Bakarna prevlaka je elektrohemijski taložena neposredno na aluminijum kao osnovna prevlaka. Nakon toga, prevlaka nikla i prevlaka bakra iz kiselog kupatila je takođe elektrohemijski taložena. Na ovaj sistem prevlaka taložena je prevlaka srebra. U radu je takođe je ispitivan uticaj fluorida u elektrolitu za direktno taloženje prevlaka bakra na strukturu završne prevlake srebra. Morfologija i strukturne karakteristike istaloženih prevlaka su ispitivane skenirajućom elektronskom mikroskopijom (SEM). Pokazano je da se srebrne prevlake mogu uspešno nanaositi kao završne prevlake na aluminijum i njegove legure sa međuprevlakama bakra i nikla.

Ključne reči: *elektrohemijske prevlake srebra, hemijska priprema, završna prevlaka, skenirajuća elektronska mikroskopija (SEM)*