



Electrochemical Deposition of Silver on Aluminum Alloys

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Abstract

Silver coatings have a very high reflection ability. To avoid their darkening from the hydrogen sulphide in the air, a thin layer of heat-resistant colorless lacquer is applied to the coatings. Silver plating is mainly used in jewelery, optics, electronics and electrical engineering. Depending on their application the thickness of the layer may vary from 2 to 24 μm . It can be done in several ways: chemical, electrochemical, contact, etc. The most common way of silver plating is the electrochemical deposition using cyanide and non-cyanide electrolytes. The cyanide electrolytes produce light, fine crystalline, dense and plastic coatings upon silver-plating. Usually silver coatings are applied with copper or nickel intermediate layer. In order to improve the de-oxidation of the aluminum surface new chemical treatment in acid – alkaline solution was applied. Our previous research shows that the presence of diamond nanoparticles in the electrolyte increase the metal deposition. Samples were prepared from electrolyte containing 10 g/l diamond nanoparticles. Their properties were compared to the properties of reference samples. The diamonds were obtained by detonation synthesis. The aim of this study is to obtain electrochemically deposited silver layer with high density, adhesion and electric conductivity on aluminum alloys substrate. The coating was directly plated without intermediate layer. Non-cyanide electrolyte composition and electrochemical parameters were determined in order to produce Ag coatings on Al alloy substrate without intermediate layer. The coating is with good adhesion, density and thickness of 14-23 μm .

Keywords: Silver plating, Aluminum alloys, Diamond nanoparticles, SEM

1. Introduction

Silver is a white, soft and plastic metal with density of 10.49 g/cm^3 and a melting point 962°C. It is chemically resistant, characterized by high electric and thermal conductivity. Among its many useful properties, silver it is recognized to have antimicrobial activity. This property is used since many centuries [1].

Silver has a positive electrode potential of + 0.80 v and that is why it reacts only with oxidizing acids. Usually silver coatings are applied with copper or nickel intermediate layer [2]. Silver-plating can be done in several ways: chemical, electrochemical,

contact, etc. The most common is the electrochemical deposition through the use of cyanide and non-cyanide electrolytes. The cyanide electrolytes produce light, fine crystalline, dense and plastic coatings upon silver-plating.

After the original patent was issued in 1840 the silver plating is still performed using a cyanide electrolyte. Many years of R&D efforts were directed at finding an alternative to cyanide in silver plating. Now there some processes that are offered. Additional work is continuing with the objective of producing full-bright silver deposits from an electrolyte as robust as the traditional cyanide process. The use of electroplated silver on electronic components is well established and continues to expand into new applications such as on waveguides for cellular

telecommunications systems [3]. Depending on the application the thickness of the layer may vary from 2 to 24 μm [4].

Also a technology of depositing silver on aluminum using cyanide baths is proposed [5]. The technology consists of several processes. The silver plating on aluminum alloys is performed using a sequence of procedures – immersion zincating, copper plating, silver striking, silver plating and antitarnish treatment. The coating is applied on space telecommunication components.

The purpose of this study is to obtain an electrochemically deposited layer of silver on aluminum products directly without an intermediate layer. The alloys contain 7 - 10 % silicon.

2. Experimental

A complex electrolyte not containing cyanide was used in the present research because of economic and environmental reasons. It is based on a compilation of electrolytes with the following composition:

- Silver nitrate (AgNO_3) - 25-30 g/l calculated as Ag
- Potassium hexacyanoferrate (II) trihydrate - $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ - 50-80 g/l
- Potassium rodanide (KSCN) - 120-150 g/l
- Potassium carbonate (K_2CO_3) - 25-30 g/l

The anode is made of lead alloy containing silver.

This type of electrolyte contributes in preparing of light, fine crystalline, dense and plastic coatings.

The substrates to be coated are made of aluminum alloy with 7 - 10 % silicon. The samples are cylinders with diameter 15 mm and length 30 mm and rectangular tiles with dimensions 25 x 30 x 10 mm (Fig. 1).

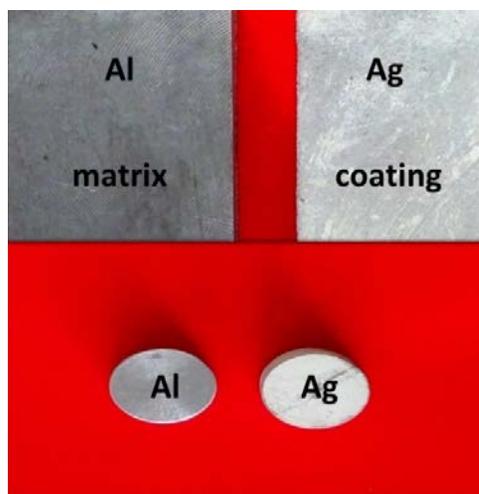


Fig. 1. Rectangular and cylindrical samples uncoated and coated with silver

The samples were degreased and then chemically treated to remove the oxide layer before the process of silver plating starts. The treatment is carried out in a mixture of nitric and hydrochloric acid for samples 7 and 8. New chemical treatment in acid – alkaline solution was applied on the surface of the samples

7* and 8* in order to improve the de-oxidation process. Our previous research [4] shows that the presence of diamond nanoparticles (NDDS) in the electrolyte increase the metal deposition. Samples 8 and 8* were prepared from electrolyte containing 10 g/l NDDS. The diamonds were obtained by detonation synthesis.

The thickness of the coatings was digitally determined by SEM investigation. Licensed analySYS software with a hardware key is used to calculate their values. Scanning electron microscope “JCSA 733” and “Zeiss EVO-10” with X-Ray micro analyser “BRUKER” was used.

3. Results and discussion

The parameters of the electrochemical process and the obtained results are presented in table 1. The temperature of the electrolyte was 20°C.

Table 1.
Characteristics of the electrodeposited silver layer on aluminum alloys

| No | ND, g/l | t, min | I, A/dm ² | L, μm |
|----|---------|--------|----------------------|------------------|
| 7 | - | 30 | 0.3 | 7.03 |
| 7* | - | 35 | 0.3 | 14.70 |
| 8 | 10 | 30 | 0.3 | 11.29 |
| 8* | 10 | 35 | 0.3 | 23.02 |

ND – concentration of diamond nanoparticles in the electrolyte, g/l;

t - duration of the process, min;

I - current density, A/dm²;

$\Delta g'$ - yield of silver, mg/cm²;

L - thickness of the coating, μm ;

*Acid-alkaline treatment of the surface of the aluminum samples before the electrochemical process.

The thickness of the coating depended on the preliminary treatment and the duration of the process. The newly proposed chemical treatment in acid-alkaline solution doubled the thickness of the coating at one and the same electrochemical conditions. The use of diamond nanoparticles in the electrolyte increases the thickness of the silver layer with approximately 60 % compared to the silver layer deposited from electrolyte without ND.

To our estimate the possible mechanism of chemical and electrochemical processes during the silver plating of the studied aluminum substrates can be the following:

1. $\text{AgNO}_3 \leftrightarrow \text{Ag}^+ + \text{NO}_3^-$ (1)
2. $\text{K}_4\text{Fe}(\text{CN})_6 \leftrightarrow 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$ (2)
3. $[\text{Fe}(\text{CN})_6]^{4-} \leftrightarrow \text{Fe}^{2+} + 6\text{CN}^-$ (3)
4. $\text{Ag}^+ + \text{CN}^- \leftrightarrow \text{AgCN}$ (4)
5. $\text{AgCN} \leftrightarrow \text{Ag}^+ + \text{CN}^-$ (5)
6. $\text{KCNS} \leftrightarrow \text{K}^+ + \text{CNS}^-$ (6)
7. $\text{Ag}^+ + \text{CNS}^- \leftrightarrow \text{AgCNS}$ (7)
8. $\text{AgCNS} \leftrightarrow \text{Ag}^+ + \text{CNS}^-$ (8)
9. $\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag}^0$ (9)

Scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) were used to characterize the silver layer deposited from electrolyte with and without diamond nanoparticles. The microstructure and microanalysis of the coating electrochemically deposited from electrolyte without diamond nanoparticles (sample 7*) are presented in figures 2 and 3. The silver layer is dense, uniform and with good adhesion. The microanalysis shows the aluminum matrix in red and the silver layer in green.

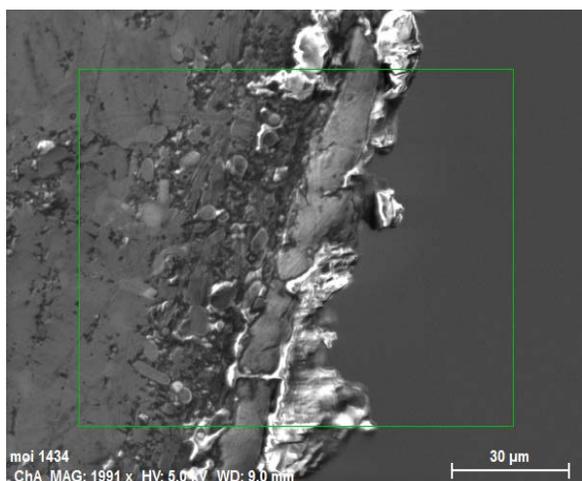


Fig. 2. Image in secondary electrons in the observed area of the silver coating on aluminum alloy (sample 7*)

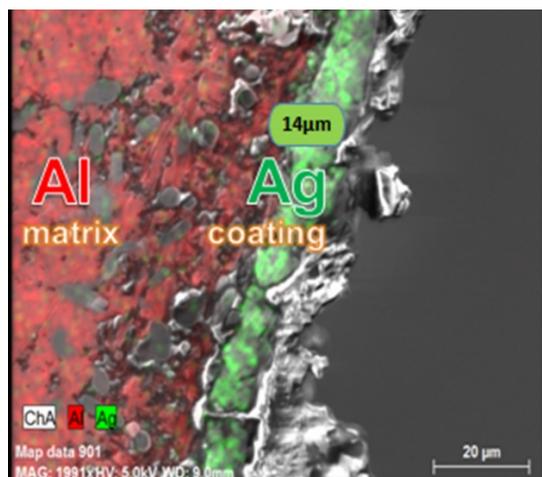


Fig. 3. Image in secondary electrons in the area of the silver coating on aluminum alloy on sample 7*, red – Al, green – Ag

The microstructure and microanalysis of the coating electrochemically deposited from electrolyte with diamond nanoparticles (sample 8*) are presented in figures 4 and 5. The microanalysis shows the aluminum matrix in red and the silver layer in blue. It also shows some carbon contamination (green areas) most probably obtained during the process of SEM sample preparation and not due to the diamond nanoparticles in the silver plating electrolyte. It is clearly seen that the diamond nanoparticles added in the electrolyte (10 g/l) contribute to the the

formation of about 60 % thicker layer compared to the layer of sample 7* (Fig. 3), which was deposited without nanodiamonds in the electrolyte. Both samples were prepared at the same electrochemical parameters of the process.

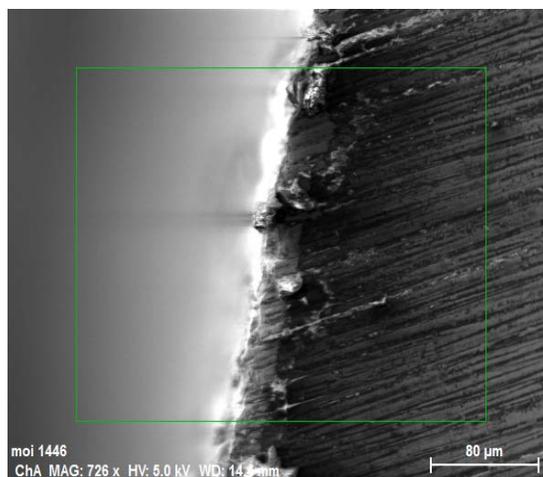


Fig. 4. Image in secondary electrons in the observed area of the silver coating on aluminum alloy (sample 8*)

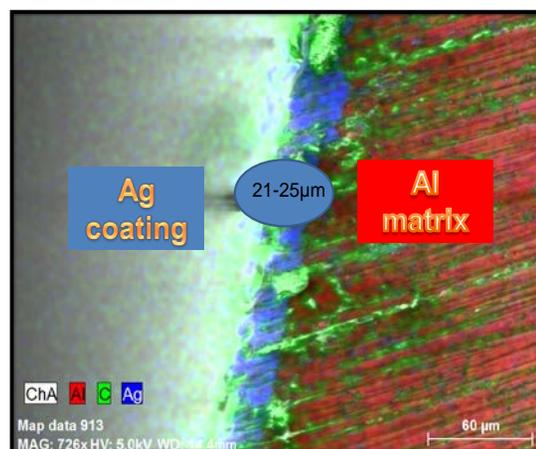


Fig. 5. Image in secondary electrons in the area of the silver coating on aluminum alloy on sample 8*, red – Al, green – C, blue – Ag

The thickness of the silver coating on aluminum alloy (sample 8*) was between 21 – 25 μm (Fig. 6). It was digitally determined with specialized software “analysis” and the average thickness was 23.02 μm. The coating is dense and homogenous with good adhesion to the substrate.

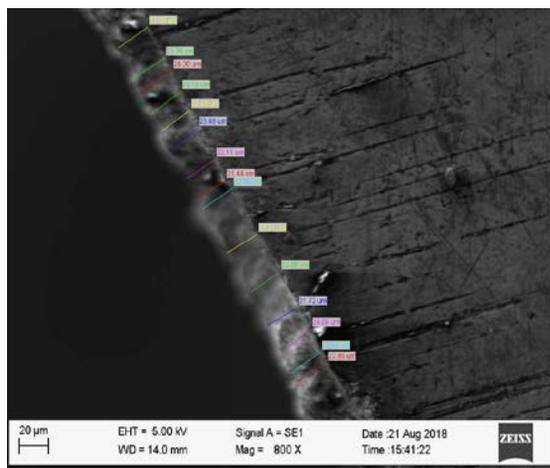


Fig. 6. Determination of the average thickness on electrodeposited silver layer on aluminum alloy (Sample 8*) - 23.02 μm . The electrolyte contains ND

The spectral analysis (Fig. 7) showed mainly peaks of silver and some other elements, but carbon peak (nanodiamond) was not observed. Therefore, the presence of diamond nanoparticles in the silver layer cannot be proven by SEM - EDS analysis. However, a significant increase in the physical and mechanical properties of the nanodiamond samples was found, the most evident it is in the intensification of the electrochemical process, leading to increase of the rate of deposition of silver on the aluminum substrate. This fact at least proves the positive effect of the diamond nanoparticles in the formation of the silver layer.



Fig. 7. Spectral analysis of the elements (SEM-EDS) of the silver layer with diamond nanoparticles deposited on aluminum substrate (sample 8*)

4. Conclusions

1. Electrolyte composition and electrochemical parameters were determined in order to produce Ag coatings on Al alloy substrate. The coating is with good adhesion, density and thickness of 14-23 μm .
2. The probable mechanism of obtaining a silver coating on aluminum alloy by the use of potassium hexacyanoferrate in the electrolyte was determined.
3. A special chemical treatment (etching) of the aluminum alloy surface was used, which allows direct electrodeposition of silver without an intermediate layer of Ni or Cu.
4. The use of diamond nanoparticles in the electrolyte increases the thickness of the silver layer with 60 % compared to the silver layer deposited from electrolyte without ND.

References

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