The Effect of Electroplating Time on Microstructural Properties and Hardness of Silver Coating on C10100 Alloy

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Abstract

In the present study, the effect of electroplating time on the intensity of flow and the constant potential difference on the thickness of the coating, surface smoothness, microstructure of the interface between substrate and coating and hardness of coating were investigated. Microstructural studies by optical microscopy (OM) showed that increasing the electroplating time leads to increase the coating thickness. Investigations showed that increasing the plating time due to growth leads to increase the surface roughness of coating. In the middle part of the coating, by increasing the time of plating, the thickness of eutectic Ag-Cu film increased. The results of microhardness of coatings showed that the maximum hardness was achieved at the highest planting time i.e 8 minutes. The microhardness remained at a constant range for about half a minute to two minutes, but increasing the time to 4 and 8 minutes leads to increase toughness of 107 and 131 Hv.

Keywords: Silver Coating, Electroplating Time, Coating Thickness, Microhardness.

1. Introduction

Silver-based coating by electroplating has special applications in electronic industries and semiconductor manufacturing [1]. Silver coatings for economic and proper electrical performance and the lack of oxidation properties can be a good alternative to gold and with continuity to copper [2]. Silver coatings have a little hardness, hence, there are several ways to improve this performance, such as reducing the grain size [3], making an alloy coating such as Ag-Bi alloy [4, 5], increasing the electroplating time to strengthen the coated layer and increasing its thickness and electromagnetic protection [6]. To control these parameters, two factors of plating time and flow intensity are important. Based on the overall conclusion of the research, the initial effect of these parameters is difficult due to the different reactions of the electrolyte system [7]. Therefore, in this study, the intensity of the flow and the potential difference were fixed to maintain the electrolyte concentration constant. The smoothness of surface of silver coating is very important for decorative and industrial applications [8]. One way to create this smooth surface is add additives like APT to an electric solution [9]. Another way is to use an electrolysis process instead of electroplating, in which ions appear by creating heat on the surface.

In the research done by Gupta and et al[10]., optimization of the silver coating parameters on Inconel 718 showed that coating thickness of silver has been controlled through optimization of process parameters like current density, bath temperature, pH, process duration, etc.

In the research done by Güler and et al[11]., Investigating the effect of flake-like morphology on the coating properties of silver coated copper particles fabricated by electroless plating showed that the coating thickness not only depends on the parameters of electroless silver plating process but also depends on the morphology of the copper particles [12].

In the present study, considering the flow intensity and the potential constant difference, the effect of plating time on the thickness of the coating, as well as its effect on the surface smoothness coated on the substrate of pure copper C10100 has been investigated.

Because the surface smoothness and hardness are important factors in the quality of the silver coating, as well as in the research done so far, the effect of electroplating time on the surface smoothness and hardness of the silver coating on the C10100 alloy have not been investigated, so the novelty of the present research can be this.

2. Materials and Methods

To conduct this research, the commercial pure copper alloy C10100 was used.

The chemical composition of the used C10100 given in Table. 1. In the first step of the desired volume,

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pieces strip-shape in the dimensions of 100×10×2 mm was prepared by an electric discharge cutter. Prepared pieces were polished in order to achieve optimal surface roughness of 1500 SiC paper.

The samples polished were washed with distilled water and acetone and then rubbed and cleaned in an ultrasonic bath. After fattening and cleaning, the samples were again washed with distilled water and then stored in a desiccator.

Table. 1. Chemical composition (wt. %) of pure copper substrate (C10100).

Cu	Fe	Pb	Zn
Balance	0.0009	0.0004	0.0001
P	Ag	As	Sb
0.0002	0.0024	0.0004	0.0004

Cleaned samples were etched by immersion method for 5 minutes for activating and receiving the best coating, by HNO_3 solution of 2 percent. After etching, the samples were washed with distilled water and quickly dried [13].

After drying, the samples were again stored in a desiccator. After the mentioned steps, samples were placed in 0.5, 1, 2, 4, and 8 minutes in silver plating bath.

The chemical composition of the used bath and the bath conditions have been given in Table. 2. and the code of the different samples based on the plating time given in Table. 3. To perform electroplating, C10100 copper was used as a cathode and pure lead as anode.

In performing plating processes, pH plays a significant role in the final properties of coating. Due to the presence of the anode, cathode and bath combination, the constant flow intensity of 0.2A and 3.2 V constant potential differences was used to pH to be remained constant. A magnetic stirrer was used to provide the required temperature and not depositing the particle of bath.

Table. 2. Chemical composition and operating conditions of Electroplating bath [12].

Chemical composition	Concentration
$AgNO_3$ (Source of Ag)	3.5 g/L
Na_2EDTA* (Complex agent)	17 g/L
EN (Complex agent)**	23 g/L
$C_4O_6H_4KNa$ (Reducing agent)	17 g/L
(dipy) , (bhpy)* (Stabilizer)**	2 g/L
Operating conditions	
pH	11
Temperature	50°C
Stirrer Speed	300 rpm
*** ethylene diamine tetraacetic acid disodium salt.** **** ethylene diamine** ****** dipyridyl (dipy) and bromo hexadecyl pyridine (bhpy)**	

Table. 3. Samples code based on different plating time.

Sample Code	Electroplating Time(min)
A	0.5
B	1
C	2
D	4
E	8

The smoothness of surface of samples' coating was examined by microprocessors at 17 mm. After coating, the morphology of the coating was investigated by scanning electron microscope (SEM) of Philips XL30 model with a voltage of 25KV.

The cross-sectional surface and the thickness of coating after polishing to SiC No. 3000, and etching in ammonia, water and $CuCl_2$ solutions were investigated by the Olympus Optical Microscope (OM).

The hardness of the samples was checked at a micro-vickers scale under a load of 200 g and a 10-second stop time. From the cross-sectional surface of each coating, five points of effect were obtained, which the average of hardness was reported.

3. Results and Discussion

In Fig. 1., the image of the coated samples has been shown. Ocular examination of samples showed the lack of crack or discontinuities in the coating. This issue suggests that selecting the parameters of this process and the bath composition is properly selected, which not leads to inconsistencies in the surface of the coating.

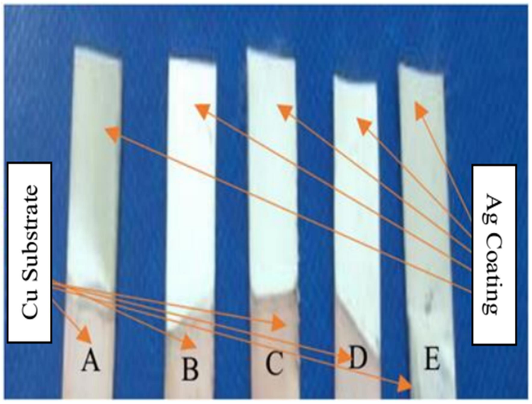

Fig. 1. Image of the appearance of coated samples.

Naturally, increase the plating time in the different potentials and the constant flow intensity follows increase the thickness of the coating layer.

By increasing plating time, the electrolyte deposition rate increases on the surface of the cathode.

By increasing the plating time, the opportunity to absorb ions is provided by the cathode. Thus, by increasing the time required for the absorption of silver ions by the cathode, the coating becomes slightly thicker [14, 15].

In Fig. 2., the trend of variations in the thickness of the silver coating is shown by increase the plating time.

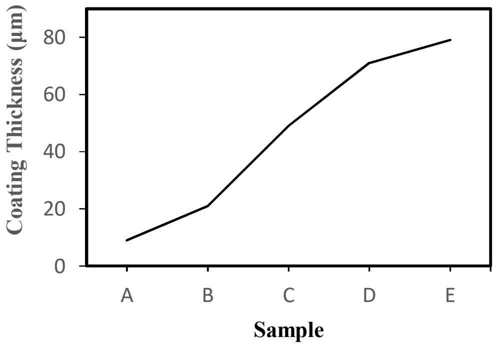

Fig. 2. The change of the coating thickness with plating time.

As shown in Fig. 2., at the time of 1 to 4 minutes, the growth rate of silver is as high as possible.

So that it can be said in the first thirty seconds and the last four minutes in the lowest possible level.

This issue indicates that it takes four minutes to reach the maximum thickness so that the rate is reasonable over time.

It seems that for more thicknesses at reasonable times, other plating baths should be used. In some references, cyanide baths have been suggested for this issue [16].

In Fig. 3., the image of OM is shown in the cross-sectional surface of the coating, which is well illustrated the trend of changes shown in Fig. 2. In Fig. 3., it can easily see the adhesion of the coating to the substrate.

This point suggests that the metallurgical bond created between the copper substrate and the pure silver coating causes the good adhesion of coating to the substrate.

In Fig. 4., SEM image of the E sample is shown. The coating morphology of sample E shows the structure of cauliflower that the typical microstructure is obtained from plating.

The cauliflower morphology due to its porous nature has the self- lubrication effect, which led to the spread of using plating method.

Substrate roughness causes germination and attaching the first silver ion to the substrate, until the next ions lie on the previous ion surface and form congresses that are similar to cauliflower or orange peel.

Each of these consists of countless seeds or nano-sized crystallites.

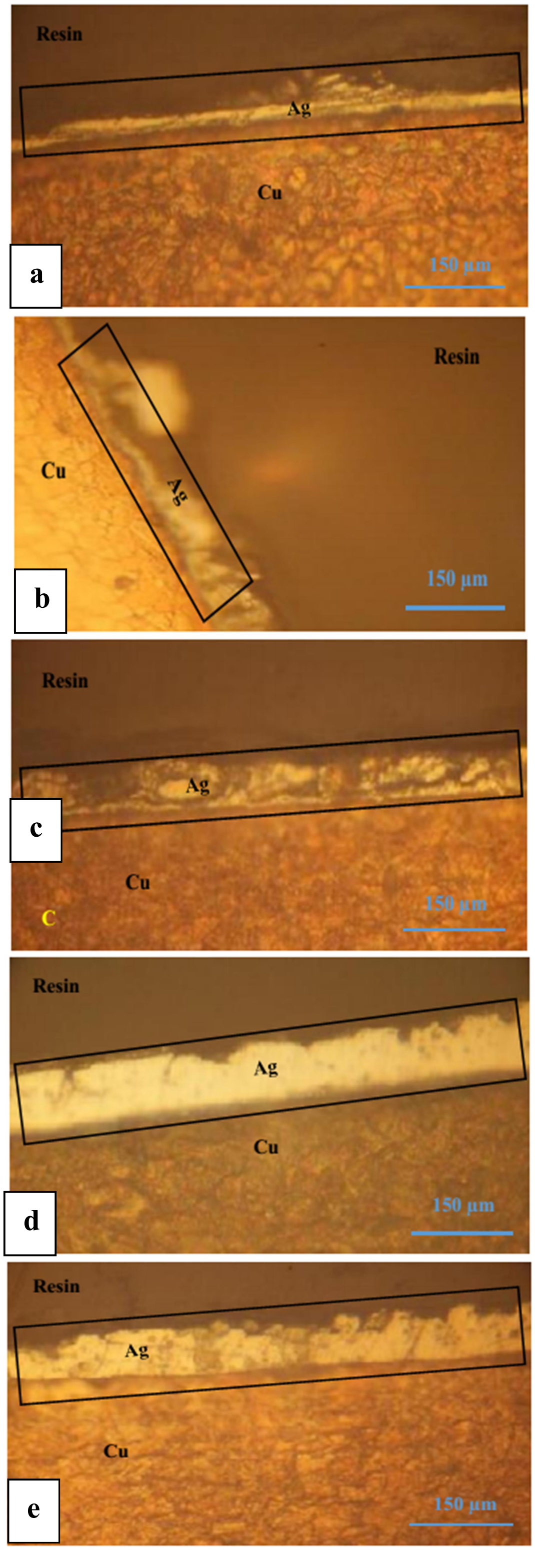

Fig. 3. Cross section showing the adhesion and uniformity and thickness of the coatings. a) Sample A, b) Sample B, c) Sample C, d) Sample D, and e) Sample E.

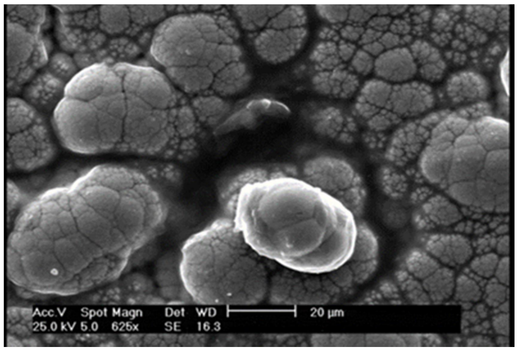

Fig. 4. SEM image of coating in sample E.

This is why, in the XRD model references, these coatings are either amorphous or contain broad and short peaks that are characteristic of a nano-sized structure. In Fig. 5., the average variations in the surface smoothness of samples have been shown due to increase the electroplating time. As shown in Fig. 5., increase the electroplating time led to an increase in the roughness of the coatings.

This is also shown in OM images of Fig. 3. In Fig. 3., it is also clear that the ups and downs of coatings have increased by increasing the electroplating time. To better understand this issue, cross-sectional images of coating of samples E and F with coating of samples A and C have been compared. Obviously, by increase the electroplating time, the thickness of the final coating, the growth rate of cauliflower increases, and the ups and downs of level increases, so the average roughness number increases. In addition, suitable places will be more to grow the structure of cauliflower, and the initial crystallites will appear as places for the growth of subsequent seeds, thus by increasing growth time and stagnation of the germination locations, a more coarse structure is achieved. This means that by increasing electroplating time, along with the increase in the characteristic of roughness or the average ups downs of coating, the average size of the cauliflower structure of the coating also increases [17].

In Fig. 6., the diagram of hardness variations is shown based on the electroplating time process.

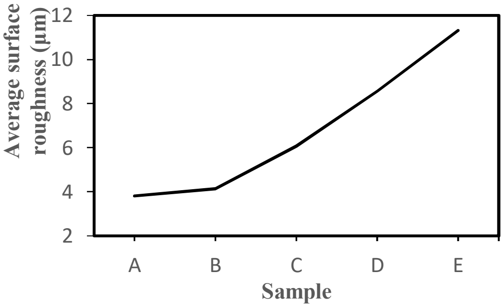

Fig. 5. Average variations of the smoothness of surface of samples R_a due to the increase of the plating time.

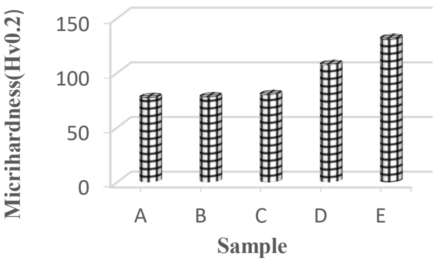

Fig. 6. Column diagram of hardness changes of samples based on the plating time.

As shown in Fig. 6., during the early times of plating, hardness has increased, but this level of increase has not been so understandable to be able to get a clear result. However, as it is clear, the hardness has increased dramatically since four minutes, so that it can be said that increase the time of plating from two minutes to four minutes resulted in an increase of hardness about 35%. At eight minutes, the hardness of the coating was increased about 22% and 64%, respectively, compared to the sample before itself, i.e sample D and the two samples before it, which four times of that time is spent for process. This point indicates that the highest hardness growth is occurred over the sample before it in the four minutes and sample D. Naturally, increasing planting time follows more thickness of coating. This increase in thickness, whether or not leads to an increase in the hardness of the deposited layer as coating. In the copper-silver dual equilibrium diagram, there is a simple eutectic transformation. Increasing the time of plating will increase the reaction time between the copper substrate and the pure silver coating. As this reaction time increases, the silver copper eutectic layer becomes thicker inside the coating. This increase in hardness due to increase the plating time can be correlated with increasing diameter of the silver-copper eutectic layer. In Fig. 7., the dual copper-silver diagram and various metallurgical regions of D are shown.

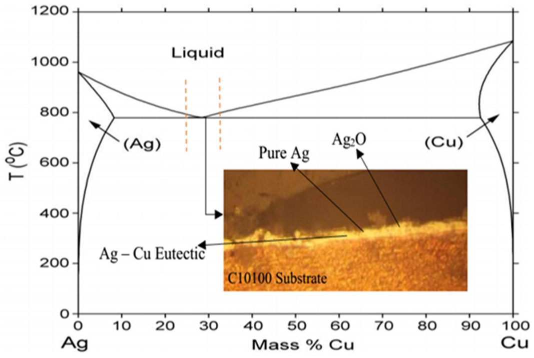

Fig. 7. Copper-silver binary diagram and various metallurgical regions of sample coating D.

By increasing plating time, the thickness of the oxide film formed over the pure silver increases. Since the hardness of metal oxide is higher than the metal itself, it is also effective in increasing the hardness of the coating [18].

4. Conclusions

From the present research, it can be concluded that:
1. By increasing the planting time, coating thickness increases.
2. The metallurgical areas of the coating can be divided into eutectic, pure silver and silver oxide.
3. By increasing the plating time in order to grow the cauliflower structure and increasing germination points, the roughness of coating surface increases.
4. Increase of planting time leads to increase the thickness of the eutectic layer, stabilize the oxide film and increase of the coating hardness.

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