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PLATING ON ANODISED ALUMINIUM

D KANAKARAJ, R VENKATACHALAM, VL NARASIMHAN and R SUBRAMANIAN

Central Electrochemical Research Institute, Karaikudi - 623 006

ABSTRACT

Laboratory scale investigations on the use of sulphuric-oxalic acid anodising bath for plating purposes are presented and the results of this bath are compared with other standard baths after plating in respect of coverage, adhesion etc. The experimental results indicate that direct plating of copper is quite possible on oxide films formed from sulphuric-oxalic acid bath with good coverage, adhesion and fairly higher thickness from an acid copper bath.

Key words: Anodised aluminium, copper electroplating, H_2SO_4- Oxalic acid bath

INTRODUCTION

A number of methods have been described [1, 2] for plating on anodised aluminium, making use of anodic coatings produced from electrolytes such as phosphoric acid, oxalic acid, chromic acid, phosphoric-sulphuric acid, sodium carbonate etc. It is generally concluded that anodising in phosphoric acid or phosphoric acid based electrolytes is the only one to provide a substrate for good adhesion [3] without any conditioning treatment. Another wellknown procedure for plating on anodised aluminium is known as Krome-Alume process [4, 5] which is based on anodising in oxalic acid. This anodic film requires a surface conditioning treatment in a cyanide or a fluoride solution to ensure good adhesion of the electroplate.

The interest on plating on anodised aluminium has been revived recently as is evident from a score of papers appearing on this subject [6 – 9]. It has been concluded [6, 9] that phosphoric acid anodising is the best suited for subsequent plating because of the large pore diameter, optimum pore density and structure of phosphoric anodised films. However, differences have been expressed on the theory of adhesive bonding of the electroplate to the porous oxide film. It is reported [6] that adherent plating on sulphuric acid anodised aluminium is possible only when the thickness of the anodic film is less than 3μ. However, in view of their high hardness and strength the coating from sulphuric acid should function well as a pretreatment for electrodeposition if the pore diameter is sufficient to allow substantial pore filling by the electrodeposit [9].

It was felt that by using a mixture of oxalic acid and sulphuric acid, the pore structure of sulphuric acid film could be modified to have large pore diameters without loss of strength of the oxide film – a requisite for good bonding strength. A printed circuit pattern of 35μm thick copper on anodised aluminium with no electrical contact between the two metals was required for an electronic instrument. It was therefore decided to have anodized film of thickness 25μ on aluminium and then plate with copper. In this paper the preliminary investigations of copper plating on anodized aluminium (2S alloy) are reported.

EXPERIMENTAL

Aluminium panels (2S alloy) [5 cm (l) x 8 cm (b)] were mechanically polished to a bright finish, degreased in trichloroethylene and soak cleaned in a dilute solution of sodium carbonate-trisodium phosphate at 60° -65°C for 2 minutes, rinsed, desmutted in 1 : 1 nitric acid, washed in running water, rinsed in deionised water and anodised in the electrolytes, the compositions of which are given in Table I.

Table – I: Composition and operating conditions of anodising electrolytes

No.	Bath	Composition	Temp. (°C)	Voltage (V)	Current density (A.dm^{-2})	Time (mins.)
1.	Phosphoric acid (85%)	15% v/v	40	30	6.0	5
2.	Phosphoric acid (85%) + Sulphuric acid (sp.gr. 1.84)	15% v/v + 15% v/v	38	13	3.3	5
3.	Sulphuric acid (sp.gr. 1.84) + Oxalic acid	7% v/v + 3% v/v	25	40	1.2	40

Anodic film was conditioned, whenever desired, in the electrolytes shown in Table II. All the electrolytes were prepared from LR grade chemicals.

Table – II: Anodic film conditioning treatments by immersion

No.	Bath type	Composition	Temp. °C	Time (min)
1,	Cyanide	6% w/v NaCN	35	10
2.	Fluoride	6% w/v NH_4HF_2	35	5

A thin film of metal was deposited on the anodized films with and without preconditioning treatment from the electroplating baths (vide Table III). This was followed by plating in acid copper bath at 2.5 A.dm^{-2} for 60 mins. with the temperature of the bath maintained at 35°C. High purity copper anodes bagged in terylene cloth were used.

Table—III: Plating bath compositions and operating conditions for initial deposition of a thin layer of copper on anodised aluminium panels

No.	Bath type	Composition (g/l)	pH	Temp (°C)	Current density ($A.dm^{-2}$)	Time (mins.)
1.	Acid copper	$CuSO_4.5H_2O$ 200 H_2SO_4 40 ml/l Glue 0.5	1 – 1.5	35	1	10
2.	Pyrophosphate copper	Copper 30 Pyrophosphate 200 Oxalate 15 Nitrate 5 Ammonia 3	8.5	50	2	10
3.	Watt's nickel (low pH)	$NiSO_4.7H_2O$ 240 $NiCl_2.6H_2O$ 45 Boric acid 30	2.5	50	5	5

Thickness of anodic films formed on aluminium were determined separately by stripping in phosphoric acid-chromic acid bath at 90°C. The surface coverage of the oxide film by initial thin layer deposits were visually examined. The copper deposit on the edges of the panels were ground off before the adhesion test was carried out. Adhesion of the electroplated copper to aluminium was tested by repeated bending of the plated specimen through 180° over a mandrel of 3 mm diameter steel rod held in a vice and then hammering it flat [10]. In case of very poor adhesion, the deposit lifted off from the panels during the preliminary grinding operation itself and could be peeled off easily.

RESULTS

The experimental observations on coverage and adhesion are given in Table IV. On phosphoric-sulphuric acid anodised aluminium, the coverage by nickel and adhesion of copper were very good with or without film conditioning treatments. Coverage by initial acid copper layer was good with film conditioning.

Table—IV: Surface coverage of anodic films by initial thin layer deposits and adhesion of copper deposit from an acid bath on anodised aluminium

Anodising bath*	Anodic film** conditioning	Initial† electro-deposit	Coverage	Adhesion
1	Nil	1	No	Very poor
		2	No	Very poor
		3	Tiny specks Poor coverage	Very poor
1	1	1	No	Very poor
		2	Poor	Poor
		3	Good	Poor
2	Nil	1	Poor	Poor
		2	Good	Poor
		3	Good	Very good
2	1	1	Good	Very good
		2	No	Very poor
		3	Good	Very good
2	2	1	Good	good
		2	Good	Poor
		3	Good	Very good
3	Nil	1	Good	Poor
		2	Good	Poor
		3	Good	Very good
3	1	1	Good	Very good
		2	Good	Poor
		3	Good	Very good
3	2	1	Good	Very good

* Please See Table I for details of anodising baths and operating parameters

** Please see Table II for details of film conditioning

† Please see Table III for initial electrodeposit's nature and operating parameters.

To ensure very good adhesion of the thick copper layer, film conditioning was essential when copper strike was used. The same trend was observed when anodising was carried out in oxalic-sulphuric acid electrolyte. Since the object was to get a thick insulating barrier between the copper deposit and aluminium, 25μ thick anodised oxide film was used. Hence the effect of film thickness from this bath on coverage and adhesion was not studied. However, we could not achieve insulation between copper layer and aluminium even with this thick anodic film as tested by electrical conductivity measurement between the top copper layer and aluminium metal. Actually. zero resistance was shown indicating probably the penetration of the bottom barrier layer by the electrodeposits. The oxalic acid-sulphuric acid anodised film could ensure an adherent electroplate with acid copper or Watt's nickel as the initial layer when a cyanide film conditioning treatment is given.

DISCUSSIONS

Studies on the coverage of an initial electrodeposit on the sulphuric acid (concentration of H_2SO_4 15%) anodised and phosphoric acid anodised films conclude [6] that the thickness of the oxide film formed in phosphoric acid does not affect the degree of coverage by copper deposit and that the high degree of coverage in these cases is indicative of high density of nucleation sites on the oxide film for subsequent plating. It is also presumed that 'the initial deposition starts at the peak around the pit groups on the anodic film'. This formation of nucleation sites is related to the retention factor of the impurity constitutents like iron present in the alloy and a chemical or electrochemical conditioning treatment of the phosphoric acid anodised film has been developed [6] to ensure excellent adhesion of the deposit on 1100 alloys. It has been shown [7] that the adhesion increases with increasing voltage, and with complete filling of the pores in the anodic films, thereby concluding that there is no penetration of the barrier layer by the plated metal.

There is a critical pore diameter below which unacceptable adhesion results and that the strength of the oxide film is a major factor in electrodeposit adhesion [8].

From the S.E.M. photographs of the anodic films on aluminium it is assumed [9] that the probable pore diameter should be around 1030 Å in 250 g/l phosphoric acid. However, the coverage on high purity aluminium was poor whereas it was complete on 7029 T6 alloy (both anodised at 20°C, 80 V in 250 g/l H_3PO_4, 20 coulombs. cm^{-2}). The pore diameter on 7029 T6 may be larger due to chemical and electrochemical dissolution of the lalloy constituents during anodising [9]. But it is not clear how the pore diameter of anodic film is influenced by the impurity contents. It has been established [9] experimentally that no only the film strength but also an 'open structure' of the film formed are necessary criteria for improving the adhesion.

The following conditions are suggested to get limiting film thickness (IFT) [9]: Phosphoric acid 250 gpl, temperature 20-25°C, current density 1-2 $A.dm^{-2}$, voltage 60 – 80 volts and time 30 minutes for 7029T6 anodising for a longer time for high purity alloys and a lower temperature with higher voltages for highly alloyed metal. It has also been established that the pore filling by the electrodeposit is essential for good adhesion.

Addition of oxalic acid to a sulphuric acid anodising electrolyte modifies the anodic film with a larger pore diameter and increase in hardness and strength. The cyanide conditioning treatment or the fluoride conditioning treatment probably attacks the surface oxide film to produce an open structure at its limiting film thickness which was reached in 40 minutes anodising time. The complete filling of the pores is ensured as is evident from zero resistance between copper layer and aluminium substrate. Thus the two essential criteria for good adhesion namely, an optimum strength/structure combination with an 'open structure' produced by surface conditioning treatments are achieved for the oxalic-sulphuric acid electrolyte runs parallel to the behaviour of phosphoric acid-sulphuric acid in this regard except that the latter does not require film conditioning treatment to ensure electroplate adhesion probably because of the pore diameter and structure is well around the optimum even without film conditioning.

In the present work it appears that the metal deposit has penetrated the barrier layer (zero resistance between copper and aluminium) whereas the earlier workers [7, 9] have concluded that there is no penetration of the barrier layer by the electrodeposit. It is to be confirmed whether the film modification treatment electrolytes have also attacked the barrier layer at the bottom of the pores while opening up the surface pores. Except for this difference, the present work makes it possible to plate very adherent deposits on anodised 1100 aluminium alloys.

CONCLUSIONS

A non-phosphoric anodising electrolyte namely sulphuric acid-oxalic acid electrolyte produces an anodic film receptive to adherent electroplates when the film is suitably modified. Copper can be deposited adherently on this modified film from an acid copper sulphate bath. Nickel can be deposited with very good adhesion from a low pH Watt's bath on this film with or without film conditioning treatment.

The behaviour of the oxalic acid-modified sulphuric acid bath is similar to sulphuric acid modified phosphoric acid bath in producing an optimum strength/structure combination at L.F.T. The work supports the mechanism of adhesion of electroplates to anodised aluminium surface due to complete filling of the pores of an open structured anodic film, but the metal deposits have penetrated the barrier also to establish a direct metallic bond with substrate aluminium. Although the main object of having an insulating layer between the copper deposit and aluminium substrate is not achieved, yet a method for plating adherent electrodeposits on thick anodised film has been found.

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