Effect of α-picoline and quinoline on dc and pulse plating of nickel directly on aluminium

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Nickel electrodeposits were formed directly on to AA 1100 aluminium alloy using a simple chemical pretreatment both by direct current plating (DCP) and pulsed current deposition (PCD) methods in the absence and presence of α-picoline and quinoline. In dc plating the current density was varied between 1 and 4 A dm^{-2}. In pulse plating, the current density was varied between 1 and 4 A dm^{-2} and the duty cycle was varied between 10 and 80% at the frequency of 100 Hz. The throwing power and current efficiency of the bath were determined. The influence of current density, duty cycle, α-picoline and quinoline on throwing power and current efficiency of the bath during direct and pulse current plating have also been studied.

Keywords: Duty cycle, Current efficiency, Throwing power, Direct current, Pulse current

Introduction

The nickel plating process is used extensively throughout the world for decorative, engineering and electroforming purposes.[1-4] In electronic applications nickel coatings are widely used as underlayers beneath precious metal deposits where nickel acts as a barrier to prevent interdiffusion of substrate and coating and additionally improves reliability of electronic components.

Electroplated nickel coatings are applied to aluminium alloys to increase the resistance to abrasion and erosion. They are thick ($\sim$250 µm or greater) and have high resistance to corrosion. Electroplated nickel coatings occasionally are also used to facilitate soldering, although other electroplated coatings generally are employed for this purpose.

The pulsed current deposition (PCD) technique[5-9] is a versatile method for preparing nanostructured metals, alloys and composite coatings. In recent years, PCD has emerged as something of a cynosure of modern technology and, thus, much attention has been paid to it globally because it is a versatile technique that, among other properties, allows the preparation of large, bulk samples with purity, low porosity and enhanced thermal stability.

Nickel plating on aluminium is very difficult because of the presence of a natural oxide film and the number of pretreatment steps that have to be conducted before electroplating. No single step pretreatment has been reported for direct plating of nickel on aluminium and its alloys. It has been the practice to protect aluminium and its alloys by modifying the surface either by the formation of a thick oxide film by anodising or by deposition of zinc/tin from zincate/stannate baths before electroplating. Anodised coatings have certain disadvantages. The oxide layer is brittle in nature and

forms an insulating layer. Reflectivity is reduced unless high purity metal is used and it has limited corrosion resistance in some environments. In the zincating/stannating process, if the surface of the substrate metal is not homogeneous, an immersion coating of different thickness will be obtained on the matrix and on intermetallic constituents. Good adhesion is achieved only if the plated articles are then heated for $\sim$30 min at 230°C to enable interdiffusion to occur. Also, the deposit obtained from a simple zincate solution will be thinner and more compact. The reproducibility of coatings on aluminium by zincating is critical and special electroplating baths may be necessary for various alloys.

In order to overcome the above drawbacks and to eliminate the number of steps involved in the pretreatment, a novel and simple chemical pretreatment has been developed for electroplating of nickel on aluminium.

Studies on nickel plating on aluminium have been reported by several authors.[10-13] But, a thorough literature survey shows, the authors believe, that no work has been reported on pulse electrodeposition of nickel on aluminium and its alloys. Therefore, the aim of the present work was to develop a simple pretreatment procedure for direct nickel plating on aluminium from a Watts nickel bath.

Experimental

AA 1100 aluminium alloy specimens of size $50 \times 20 \times 0.1$ mm were prepared and mechanically polished to obtain a surface roughness of 0.1 µm. The polished specimens were degreased with trichloroethylene and chemically treated in a specially developed simple pretreatment solution containing 10 g dm^{-3} of nickel chloride, 50%(v/v) orthophosphoric acid and 5%(v/v) hydrochloric acid at 30°C for 5 min. After rinsing in deionised water, the specimens were electroplated from a conventional Watts nickel bath. The composition of the bath is given in Table 1.

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Quinoline

CH₃
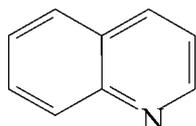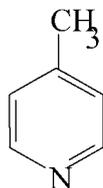
α-Picoline

1 Structures of additives quinoline and α-picoline

Both direct current and pulse current were used for electrodeposition.

Pulse electrodeposition was performed at 40°C for 15 min using a Kraft Dynatronix DPR 20-5-10 model pulse equipment, and in the case of dc electrodeposition was carried out for 30 min. For the determination of throwing power, a Haring–Blum cell was used and the plating was carried out for 10 min in the case of dc and 5 min in the case of pulse plating. The current density was varied between 1 and 4 A dm^{-2}. Pulse duty cycles were varied between 10 and 80% at constant pulse frequency of 100 Hz. The pulse parameters used are

Table 1 Watts nickel plating composition

	Level
Nickel sulphate, g dm^{-3}	240
Boric acid, g dm^{-3}	30
Nickel chloride, g dm^{-3}	45
pH	3

Table 2 Plating pulse data

Duty cycle, %	Pulse frequency 100 Hz and pulse on–off times, m s
10	1–9
20	2–8
40	4–6
60	6–4
80	8–2

given in Table 2. In order to produce a bright nickel deposit with fine grained nature and improved throwing power, both dc and pulse plating were carried out in presence of 0·1% α-picoline(C_6H_7N) and quinoline (C_9H_7N) (structures are given in Fig. 1). Adhesion of the dc and pulse nickel deposits were tested by bend and heat treatment methods. Current efficiency and throwing power of the nickel electrodeposition were measured.

Results and discussion

Adhesion test

From the bend test, it was observed that the nickel coating did not undergo any peeling from the substrate which indicates very good adhesion of the deposit. Such adhesion of the nickel deposit is further confirmed by the heat treatment test where after heating the nickel coated aluminium at 300°C for 4 h and quenching in water, no blisters were noticed.

Current efficiency and throwing power

The values of current efficiency and throwing power at various current densities in the absence and presence of α-picoline and quinoline for the dc plating of nickel on aluminium are presented in Table 3 and those of pulse plating at various duty cycles and current densities are given in Table 4. The influence of duty cycle, current density and additives on current efficiency and throwing power are discussed below in detail.

Effect of pulse duty cycle on current efficiency

The values of current efficiency for various pulse duty cycles at the constant current density of 2 A dm^{-2} are given in Table 4. From these data, it is seen that as pulse duty cycle increases, the current efficiency of the nickel deposition increases. The current efficiency can be affected by adsorption of hydrogen at the cathode during plating along with nickel deposition. At lower duty cycles, the off time is sufficient for readsorption of desorbed hydrogen gaseous molecules at the cathode and so the effect of desorption will be less; while at higher duty cycles, the effect is highly pronounced and hence lower current density is observed. Maximum increase in current efficiency has been observed at 80% duty cycle at the average current density of 2 A dm^{-2}. Increase in current efficiency must be due to the preferential reduction of adsorbed monolayer of Ni^{2+} with pulses of charges equivalent to the reduction of this monolayer, hydrogen evolution occurs preferentially after consumption of this monolayer and thus current

Table 3 Throwing power and current efficiency of dc nickel plating at various current densities with and without additives

Current density, A dm^{-2}	Without additive		With α-picoline		With quinoline	
	Throwing power, %	Current efficiency, %	Throwing power, %	Current efficiency, %	Throwing power, %	Current efficiency, %
1	15·0	84·5	18·9	85·7	16·1	85·1
1·5	21·9	86·3	22·7	88·9	22·5	88·2
2	23·7	88·2	27·6	93·2	24·4	92·7
2·5	21·6	87·5	25·8	92·1	22·3	91·6
3	17	86·3	22·0	90·4	19·1	89·7
4	15·3	84·3	21·0	89·4	16·2	88·6

Table 4   Throwing power and current efficiency of pulse nickel plating at various current densities and duty cycles with and without additives

Current density, A dm^{-2}	Duty cycle, %	Without additive		With α-picoline		With quinoline	
		Throwing power, %	Current efficiency, %	Throwing power, %	Current efficiency, %	Throwing power, %	Current efficiency, %
1	10	16·5	86·1	19·8	86·9	19·5	86·3
1·5	10	22·3	86·8	23·8	87·6	23·1	87·2
2	10	24·3	89·3	24·8	89·7	24·0	89·4
2·5	10	22·6	88·1	23·7	88·9	23·1	88·6
3	10	18·5	87·5	19·0	88·1	18·5	87·9
4	10	16·6	85·7	21·9	86·2	21·4	85·9
2	20	11·6	83·2	12·3	83·8	13·1	83·5
2	40	14·2	89·7	15·1	90·3	16·8	89·9
2	60	19·9	92·1	20·3	92·9	21·8	92·5
2	80	24·0	93·3	24·4	94·7	24·8	93·9

efficiency decreases for increasing pulse duty cycle in the case of high frequency pulse plating.[14]

Effect of pulse duty cycle on throwing power

The variation of throwing power with pulse duty cycle is given in Table 4. From the table throwing power was found to increase with increase in pulse duty cycle. A maximum throwing power is obtained at higher duty cycle (80%). Because at lower duty cycle, off time is very high, the established equilibrium concentration is once again disturbed and so uniform deposition throughout the surface cannot be expected at lower duty cycle. On the other hand at higher duty cycle, the off time is exactly sufficient to establish the equilibrium concentration which ensures uniform distribution of metal ions from the bulk of the electrolyte to peaks and crevices of the cathode surface which leads to uniform deposition over the entire surface irrespective of the shape and size. Therefore, throwing power is very high for pulse plating with higher duty cycle. Maximum throwing power is obtained at 80% duty cycle for the average current density of 2 A dm^{-2}.

Effect of current density

Effects of current density on current efficiency and throwing power are presented in Tables 3 and 4 for dc and pulse plating respectively. From the tables, it is observed that the current efficiency and throwing power increase with increase in the current density up to a maximum of 2 A dm^{-2}; beyond that it remains constant or decreases. Maximum values are obtained at 2 A dm^{-2}. Normally current efficiency is known to increase with increase in nickel ion concentration in the bath. At low current density, the current passed is not entirely used for depositing nickel. Some amount of current is used for bringing the electrode potential close to that of base metal. Very high current density leads to the formation of a powdery or burnt deposit and hence current efficiency and throwing power are low.

In pulse plating especially at higher frequencies, there may be two different diffusion layers: one near the cathode surface layer is called the pulsating layer, and the other beside this is essentially stationary after a number of pulses have been applied. The inner pulsating diffusion layer thickness corresponds to pulsed current density and the outer stationary diffusion layer corresponds to average current density. This average current density is proportional to concentration gradient in the stationary layer. As the thickness of this stationary diffusion layer is an important variable in determining the rate of the electrodeposition process, if the thickness of this layer is less, more metal ions will be diffused through this layer from the bulk electrolyte to the cathode surface. At very high current densities the thickness of this layer is also very high. Thus, the number of ions transported through this layer is less which leads to lower deposition rate, and at very high average current densities deposits with poor quality are obtained. Maximum values of good quality deposits are obtained at 2 A dm^{-2}.

Effect of additives (α-picoline and quinoline)

Addition of α-picoline and quinoline to the nickel plating bath has no significant effect on the properties of the deposit. Their effect on current efficiency and throwing power for dc and pulse plating are presented in Tables 3 and 4 respectively. There is a slight increase in current efficiency and throwing power. But smoothness and brightness of the deposit increase to a larger extent. This is because picoline and quinoline are classified as second class brighteners by the presence of an unsaturated group C=N in the molecule.[3] The electrodeposition of nickel in the bath with organic additives may be explained on the basis of the ability of the hydroxide ion to adsorb onto the electrode surface or to form complexes with the depositing metal ions. According to electrobrightening theory, a bright coating is said to be produced when a layer of colloidal particles formed near a cathode is captured by a catalytically generated hydrogen film. Because of the presence of hetero atoms (N and O), they get easily adsorbed on the cathode and this increases the cathodic polarisation which can facilitate catalytic generation of hydrogen, necessary for the production of bright coatings.[15] Of the two additives, α-picoline has a more pronounced effect on brightness of the deposit than quinoline and the values of current efficiency and throwing power are higher for α-picoline than for quinoline.

Conclusions

Dc and pulse electroplating of nickel directly onto an aluminium substrate was carried out using a novel single pretreatment in a Watts nickel bath at various pulse duty cycles and current densities without and with additives α-picoline and quinoline. The throwing power and current efficiency of the baths were also determined.

It was found that the current efficiency and throwing power of the nickel bath increased up to 2 A dm^{-2} and decreased beyond that current density in the case of both dc and pulse nickel plating. There is a slight increase in current efficiency and throwing power with the incorporation of these addition agents. Of the two addition agents, α-picoline is more effective in both dc and pulse nickel plating. The current efficiency and throwing power values are higher for picoline than those when using quinoline.

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