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Periodic reverse current electroplating and surface finishing

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Using an alkaline cyanide bath at 20–90° C and periodic reverse (PR) current results in brilliant, level, and bright electroplated copper on any conventional metal substrate. The quality of the electroplate was evaluated by measuring the surface roughness and brightness. The surface roughness increases with frequency and amplitude of the PR current used for the plating. Increasing the bath temperature leads to brighter surfaces up to 50° C; higher temperatures have only a slight effect on brightness. The increase of cathodic-to-anodic period per plating cycle leads to a maximum brightness at PR ratio, cathodic/anodic, of 2 at 0·27 Hz. As the electrode separation decreases the brightness increases.

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1. Introduction

PR electroplating is one of several methods of plating with modulated current which is finding wider application for a variety of purposes [1]. This process occurs with less concentration polarization than that during electrolysis at a constant current [2]. The wave form of the current used for the PR plating is shown in Fig. 1. The anodic period of the electrolysis cycle is long enough for a certain part of the previously deposited metal to be dissolved.

Electroplating using the PR technique permits the use of higher current densities. Moreover, modified electroplate surface properties are obtained.

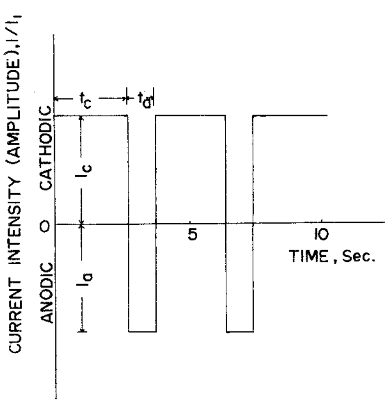

Fig. 1. Wave form of periodic reversal cycle: t_c, negative time; t_a, reverse time; I_c, strength of cathodic current; I_a, strength of anodic current.

The optical properties of the electrode surface were conveniently studied by the difference in relative reflectance. The relative reflectance change is

$$\Delta R/R = (R_2 - R_1)/R_1$$

where R_1 and R_2 represent, respectively, the reflectance of surface before and after electroplating [3]. For the sake of simplicity in the present work the reflectance after PR plating is considered as a measure of brightness as the initial surface reflectance is constant. The surface reflectivity was measured by a photoelectric cell using various angles of incident light. The maximum reading of the photocell fixed at a certain distance from the specimen was considered as an index of surface brightness.

2. Experimental procedure

The cell and circuit are shown schematically in Fig. 2. The plexiglass cell employed has a rectangular shape of size 2·5 x 10 x 12 cm. The current used in the electroplating process is first passed through a PR disc. The surface area of this disc is divided into two insulated conducting sectors which correspond to the required PR ratio (t_c/t_a). This disc is coupled to a variable speed motor which enables the use of different frequencies of electroplating cycle (0·27–1 Hz). The PR current

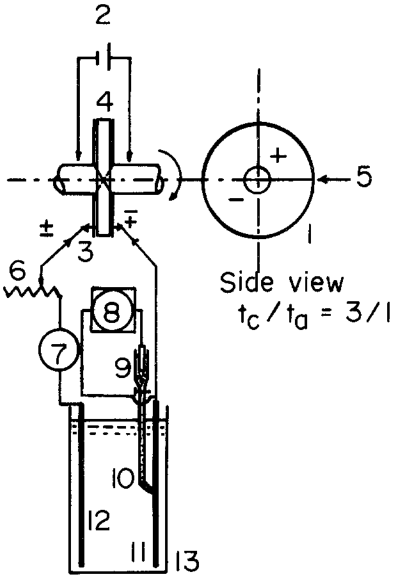

Fig. 2. Cell and electric circuit (schematic): 1, PR disc; 2, d.c. supply; 3, PR output current; 4, insulated disc fixed on an insulated shaft (coupled with multispeed motor); 5, insulated conducting copper plate sectors; 6, rheostat; 7, ammeter; 8, potentiometer; 9, reference electrode (SCE); 10, Luggin capillary; 11, copper or stainless steel (18–8) electrode; 12, electrolyte (alkaline copper cyanide); 13, plexi-glass cell.

used is transmitted from the rotating disc via conducting metal contacts that touch both of the oppositely charged face and back surfaces of the disc. The cell was operated at a constant current density; the value was (0·3–1)I_L, the limiting current density. The limiting current density was obtained for each set of conditions from conventional current versus potential curves [4]. The net plating time was five minutes.

The electrolyte used was 1·25 M copper cyanide and 0·125 M sodium cyanide. All chemicals were reagent grade and doubly distilled water was used to prepare the stock solution. The height of the electrolyte level and the distance between the two electrodes (electrode separation) were adjusted in order to have a height : electrode separation of 1·25 : 5. Electroplating was carried out in two experimental modes, one without reversing the current and the other with PR current at a certain frequency. In all the experiments fresh electrolyte was used and the same quantity of electricity was used in electroplating. The bath temperature was kept constant at 20–90° C ± 0·5° C using a thermostat.

The electrodes used were commercially pure electrolytic copper (99·9%) of height 15 cm and thickness 1 mm. The electrodes were mechanically polished with a series of abrasive papers to 600 grade, washed with distilled water and alcohol, then dried with air. After electroplating the electrodes were again washed and dried in the same manner. The surface brightness was evaluated by measuring the maximum surface reflectivity via a photoelectric cell, using various angles of incidence of light. The corrosion resistance of some electroplated copper on stainless steel (18–8) electrodes was determined by immersion of the plate in a 0·1 N nitric acid solution at 20° C. The time passed before the breakdown of the plate depends on the plate thickness and porosity and is considered as an index of corrosion resistance.

3. Results and discussion

The operating parameters for the PR plating of copper from a cyanide bath were studied. Fig. 3 shows the variation of surface roughness (peak-to-valley) of the electroplate as a function of PR current amplitude. These curves indicate that increasing the current density increases the surface roughness for a frequency of 0·67 Hz but for the lower frequencies (0·27 and 0·4 Hz) there is an increase in surface levelling (decrease in surface roughness) reaching a peak value at the current intensity of 0·8 I_L. For the same current density the deposit increases in surface roughness with an

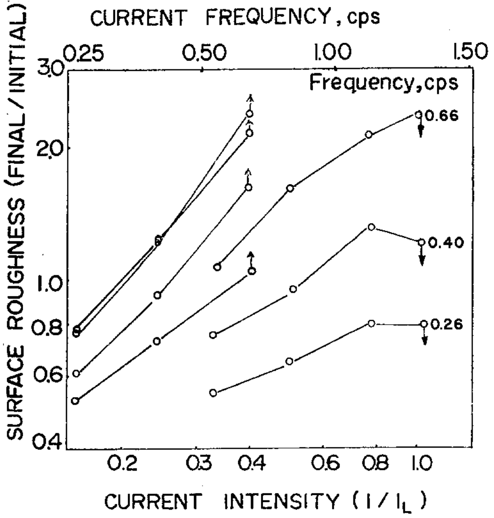

Fig. 3. Effect of PR current (amplitude and frequency) on surface roughness. Bath temperature, 25° C.

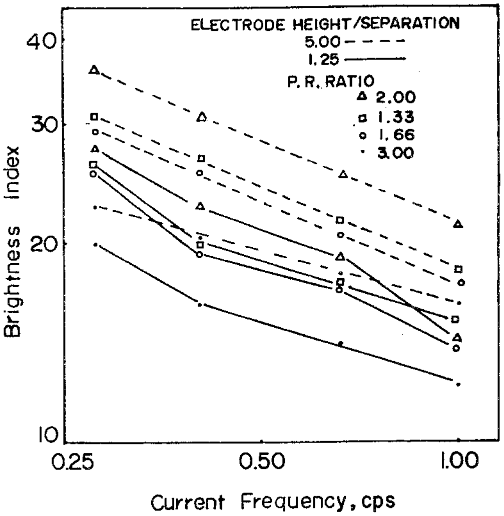

Fig. 4. Effect of PR current frequency on brightness index. Electrode height 10 cm, temperature 25° C, separation distance 2 cm.

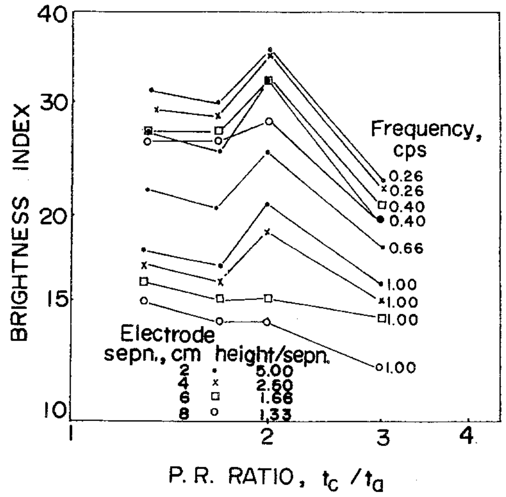

Fig. 6. Effect of PR ratio (t_c/t_a) on brightness index. Electrode separation 2 cm, temperature 20° C.

increase in frequency. The effect of PR current frequency on surface brightness is shown in Fig. 4. As the current frequency increases, the surface brightness decreases. This may be attributed to the increased rate of mass transfer at higher amplitudes and frequencies which is similar to the effect observed with vibrated copper cathodes [5]. Surface brightness increases as the electrode height: separation increases as shown in Fig. 5. There is a peak at a PR ratio (t_c/t_a) of 2 in Fig. 6. At this PR ratio it seems that an optimum deposition–dissolution ratio is obtained for forming a homogenous plate of fine grained structure; this is confirmed by microexamination of these plates. It is also possible that some preferred orientation of the electrodeposits may occur at this PR ratio.

The bath temperature plays a very important role in producing bright electroplates particularly in conventional d.c. plating. As shown in Fig. 7 at bath temperatures above 60° C there is a slight effect on brightness of the PR plate but the bright-

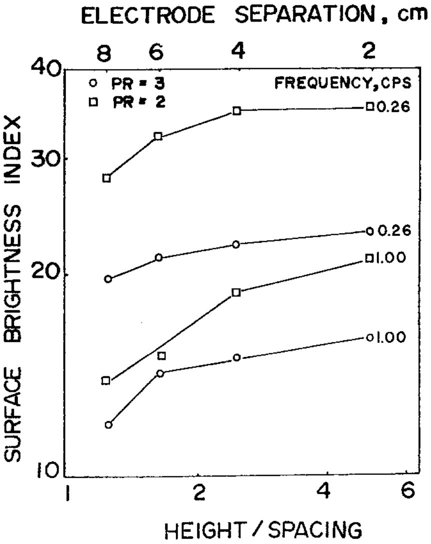

Fig. 5. Effect of electrode separation on brightness index. Electrode height 10 cm, temperature 20° C.

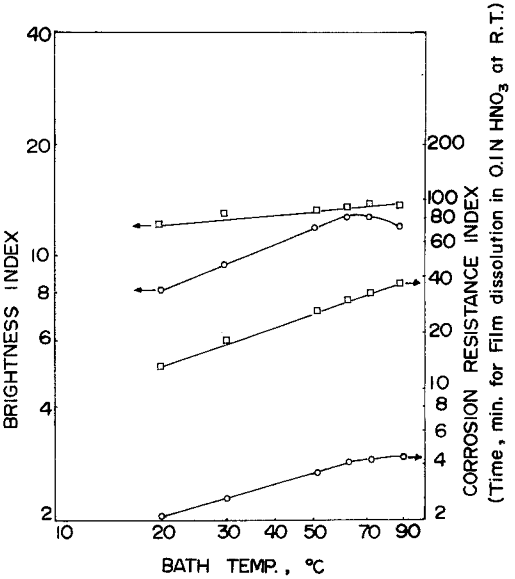

Fig. 7. Effect of bath temperature on brightness index and corrosion resistance of electroplate of copper on stainless steel. □ PR plating (PR = 1·33), ○ conventional d.c. plating. Electrode height 12 cm, width 2·5 cm, bath temperature 20° C, electrode separation 8 cm, 18 A h dm^{-2}.

ness of the conventional d.c. plate decreases. However, the corrosion resistance and possibly film thickness increase at a higher rate for the PR plate. The deterioration in the quality of the surface at high current intensities may be related to the adsorption on the electrode surface of certain ions [2].

Surface reflection of light from metal surfaces can be used to identify oxide film phases [6, 7]. The anodic film formed on copper was identified by light and electromicroscopic studies to consist of two phases: Cu_2O (cubic) and CuO (monoclinic) [8, 9]. Since during PR plating the surface is periodically anodic and cathodic, there is a possibility that the surface is partially covered by oxide film affecting the surface brightness.

4. Conclusions

The use of surface reflectivity for the investigation of PR plating of copper from an alkaline cyanide bath seems to be a very simple and promising approach, which yields experimental information relevant to problems in electrochemistry as well as to surface physics. However, the rather complex interconnection between the observable reflectance and the physical parameters of interest is a limitation of this method.

The experimental data shows the following:

(a) The surface roughness of the electroplate increases with increase of amplitude and frequency of the PR current.

(b) The surface brightness increases with a decrease in PR frequency.

(c) Brightness decreases with an increase in electrode separation.

(d) A PR ratio of two, gives the best surface brightness.

(e) An increase in bath temperature above 50° C is followed by a slight increase in brightness but the corrosion resistance of the plate decreases.

(f) The PR plate is brighter and has a higher corrosion resistance than the corresponding ordinary d.c. plate.

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