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Electroplating of Black Nickel: Bath Age and its Effect on Coating Quality

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Black nickel coating is commonly electroplated onto various substrates, including ferrous and non-ferrous metals/alloys, as a decorative layer to provide uniform black appearance. In the black nickel-plating process, nickel and zinc are co-plated out of plating bath with different ratios, leading to difficulty and complexity in bath maintenance by using soluble anode. In practice, an inert anode is used with regular replenishment to control the bath composition and pH value in the optimal ranges. Hence, as the plating bath ages and the plating bath composition changes due to the unequal consumption of nickel and zinc, the deposited coating will no longer appear black. Boric acid is frequently used as a pH buffer to stabilize the pH value of the plating bath to produce black coating with minimal bath maintenance. However, disposing the used plating bath is often expensive and incurs environmental damage when not properly disposed. In this work, a boric acid-free black nickel coating process is systematically investigated during electroplating onto copper substrates, in terms of plating bath chemical composition and pH value, on the deposited coating appearance and coating composition, to arrive at a process map indicating suitable process window for optimum black nickel coating.

1. Introduction

Black nickel coating is commonly electroplated onto various substrates as a decorative layer to provide uniform black appearance. Black nickel coatings have been widely studied when coated onto brass [1], stainless steel [2-4] and copper [4-5]. While various formulation and approaches have been shown to produce consistently black nickel plating on various substrates, not much work was done to study the effect of bath age and its effect on coating quality.

In the black nickel-plating process, nickel and zinc are co-plated out of plating bath with different ratios as the bath is being consumed. This leads to difficulty and complexity in bath maintenance by using a soluble anode. In practice, an inert anode is used with regular replenishment to control the bath composition and pH value in the optimal ranges. Hence, as the plating bath ages and the plating bath composition changes due to the unequal consumption of nickel and zinc, the deposited coating will no longer appear black and will appear defective, such as being silvery in appearance. This makes the coating less black when the bath is heavily used without regular replenishment.

The existing processes investigated in the literature use boric acid as a pH buffer to stabilize the pH value of either the plating bath [3] or in the nickel undercoat bath [4-5]. Disposing the solution is often expensive and incurs soil toxicity [6] when not properly disposed. Doing away with boric acid makes it difficult to maintain the pH value to produce consistently black coating.

Most of the current literature considers how process parameters affect the coating quality while ignoring the aspect of bath age/maintenance. Here we investigate the effect of bath age on coating quality using a boric acid-free black nickel coating process. This work shows that pH value is a key factor affecting the black nickel coating appearance. The data obtained was utilised to arrive at a process map indicating suitable process window for optimum black nickel coating.

2. Experimental

2.1 Materials and Techniques

Copper panels of size 100 x 65 x 3 mm were selected as the substrate material for this work. Before the electroplating process, each panel was weighed using a precision mass balance to an accuracy of 0.1 mg. Next, polyester tape was used to mask each panel carefully to control the exposed copper surface for plating. The plating region was controlled to be around 0.5 to 1.0 dm^2 in this work.

The copper panel was then degreased by immersion into a hot alkaline cleaning solution at 80 °C for 10 minutes. Each substrate was then rinsed using fresh deionised water, before being dipped into 10% sulfuric acid to activate the copper surface by removing the copper oxide for good adhesion of the plating in the subsequent step. The substrate was then thoroughly rinsed with deionised water. Water break test was done to ensure the copper surface is contaminant-free.

2.2 Electroplating Process on Copper Substrate

The formulation used for black nickel electroplating follows that given in Military Specification MIL-P-18317 [7] and is shown in Table 1. Before the first substrate was electroplated, the bath pH value was adjusted by addition of 28% ammonia solution to pH 6.0 as measured using a pH meter (Metrohm 826 pH mobile). The bath pH value was not adjusted subsequently in order to study the natural pH fluctuations when no bath maintenance was done. The accumulated ampere-hour (AAH) was used as a measure of the bath age. The AAH, pH value, nickel and zinc concentrations of the bath were monitored at selected intervals.

Table 1 Formulation of black nickel electroplating solution

Chemical	Amount (g/L)
Ammonium nickel sulphate hexahydrate ($(NH_4)_2SO_4.NiSO_4.6H_2O$)	60
Zinc sulphate heptahydrate ($ZnSO_4.7H_2O$)	7.5
Sodium thiocyanate (NaSCN)	15
Deionised water	Balance

The current density, plating duration, and temperature were kept constant; these parameters are shown in Table 2. Current density was controlled by presetting the DC rectifier (Extech Quad Output DC Power Supply) with the appropriate current based on the individual sample's exposed surface area. Plating temperature was controlled by immersing a thermocouple into the solution throughout the plating duration and presetting the hot plate with the appropriate temperature.

Table 2 Experimental input parameters

Input	Remarks
Initial pH (for first coating only)	pH 6.0
Current density	0.2 A/dm^2
Plating duration	20 minutes
Temperature	25 °C

When performing the plating, the copper substrate was connected to the DC rectifier and immersed "live" (current switched on before immersing) into the plating bath. A 1-litre glass beaker was used as the plating bath container and a platinised titanium mesh served as the anode.

After plating for 20 minutes, the rectifier was switched off and the sample removed from the plating bath and cleaned thoroughly with deionised water, before drying with a compressed air gun. The plated sample was then weighed again to obtain the mass of the plating deposit. The pH of the plating solution after each coating was also recorded.

2.3 Coating Evaluation

As a decorative coating, the appearance of the black nickel coating is the key factor. Each sample was first visually inspected for any defects, including localized discolorations, pinholes and burns. Next, a sphere spectrophotometer (X-rite Ci60) was utilized to quantify the colour of the coating. The spectrophotometer was used to illuminate the coating with a fluorescent light source and the reflected light was collected to produce three values, L for lightness (0 is absolute black, 100 is absolute white), while a and b denote the red/green and blue/yellow values respectively [8]. L value of below 40 corresponds to a visually dark surface.

To measure the chemical composition of the plating bath, titration was performed using an autotitrator (Metrohm 905 Titrando) on the extracted plating solution to measure the nickel and zinc concentrations. A scanning electron microscope (Jeol IT300LV SEM) coupled with an energy dispersive X-ray spectroscopy detector (Oxford Instruments X-MaxN EDX detector) was utilized to study the elemental composition of deposited coatings on selected samples.

3. Results

In this work, two sets of coatings were produced from two sets of plating solutions conducted by two operators- Operator A and Operator B. As multiple copper substrates were coated using the same plating bath without bath maintenance, AAH was used as a measure of the bath age, to quantity the mass of coating deposited for the same bath. It is the cumulative summation of the product of surface area, current density and coating duration for all coatings produced using the same plating solution. Higher AAH indicates more coatings were produced using the same plating solution. Both operators continued sequential plating until the coating colour is greyish.

Visual inspection of all samples shows no visual defects, but the coatings were found to turn increasingly grey as the AAH increased. The spectrophotometer showed the L value increased from 29.07 to 52.81 in Figure 1, corresponding to the greyer coatings as the bath was more heavily used. At the same time, only small fluctuations were detected in a and b. Figure 2 shows the optical images of selected coatings exhibiting a range of L values.

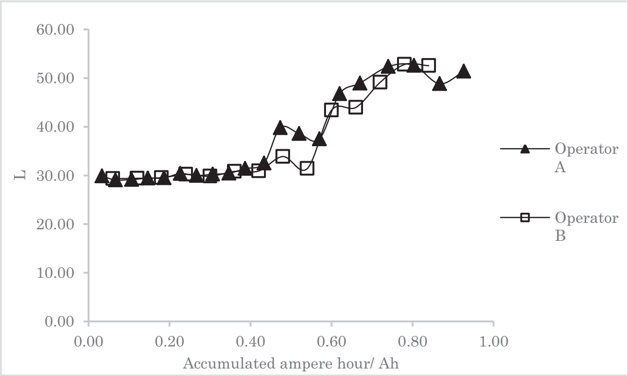


Figure 1. L value of deposited coating against the bath's AAH.

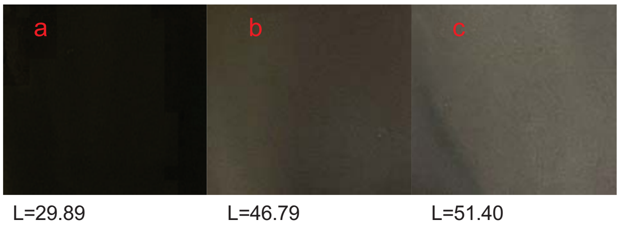


Figure 2. Optical images of selected coatings with different L values.

EDX analysis of the deposited coatings revealed more nickel is deposited than zinc at high AAH, as shown in Figure 3. Nickel is preferentially deposited over zinc as the main constituent of the coating as the AAH increased more than 0.4 Ah. A decrease in the oxygen content of the deposited coating was observed with AAH > 0.4 Ah.

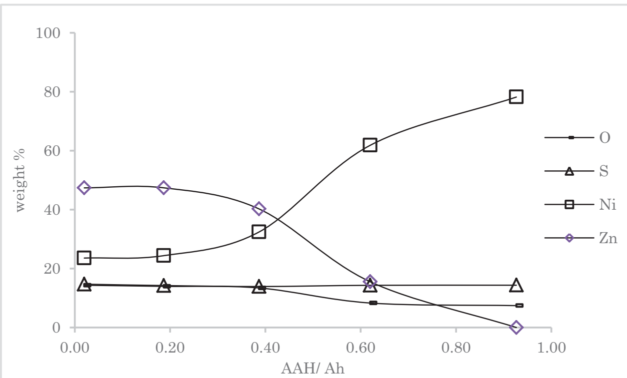


Figure 3. Elemental composition of deposited coatings against AAH.

Notably, Figure 1 shows the L value of the coatings produced by both operators show a consistent value of around 30 from 0 Ah to 0.42 Ah, before it increased steadily to around 50. This trend is supported by the small reduction of zinc to nickel ratio from 2.04 to 1.94 and coincides with a significant decrease in pH to 4.93.

Chemical analysis obtained from titration revealed the major species of zinc and nickel decreases at a much slower rate than the colour changes suggest. Plots of zinc and nickel concentration against AAH are shown in Figures 4 and 5. Through the linear regression equations, the extrapolated x-intercepts give AAH values of 2.53 and 24.6 Ah, indicating a much higher AAH than what was investigated in this work is required to fully deplete the major species in the plating bath if depletion is assumed to be linear. The titration results show that while both major species (Ni^{2+} and Zn^{2+}) were present in the plating solution, the decreasing pH value prevented their co-deposition and thus greyish coatings (predominantly Ni) were produced at high AAH.

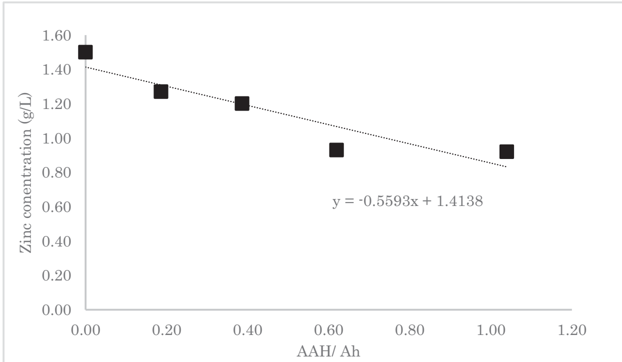


Figure 4. Zinc concentration of bath against AAH.

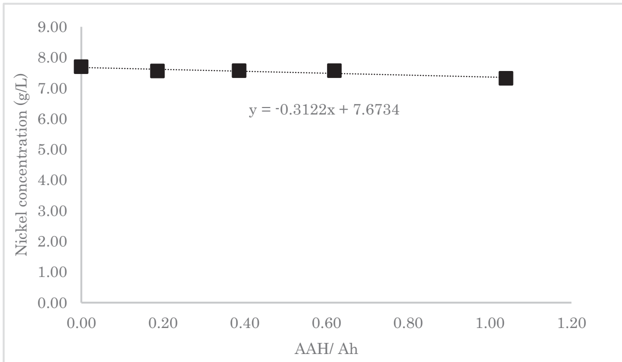
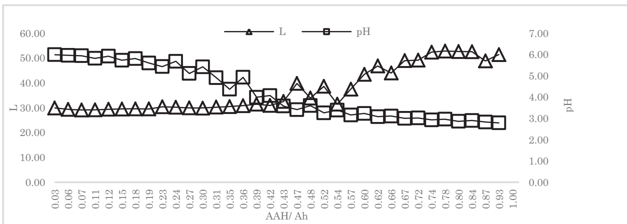


Figure 5. Nickel concentration of bath against AAH.

4. Process Map

Figure 6 shows the L-pH-AAH process map. The pH of the plating bath decreased from 6.0 to around 3.0 as more coatings were applied. The results show that a high pH (such as during low AAH) is a key



requirement to producing blackish coating of low L value.

Figure 6. L-pH-AAH process map.

Figure 6 shows that when the pH was above 5.5 and AAH was below 0.2Ah, optimal black coating of L less than 30 could be obtained. When pH was reduced to 4.5 and AAH to 0.4Ah, a highly black coating could still be obtained, where L is less than 40.

The transition zone from black coating to greyish coating took place around 0.4 Ah to 0.7 Ah while the bath pH transitioned from near pH 6 to pH 3 around 0.25 Ah to 0.5 Ah. This indicates that the pH drop precedes the degradation of the coating appearance and can be used as an early warning sign to do bath maintenance. From the results obtained, it appears that as long as the bath maintenance is done while the bath pH > 4, coating appearance should not be affected.

5. Conclusions

A boric acid-free black nickel coating process was systematically investigated during electroplating onto copper substrates, in terms of plating bath chemical composition and pH value, on the deposited coating appearance and coating composition.

The quality of black nickel coating on copper substrates was found to degrade as the plating bath was used continuously. The pH value of the chosen bath chemistry decreased significantly in the absence of a pH buffer such as boric acid, while still having adequately high concentration of key chemical species.

The L-pH-AAH process map provides a visual indicator to uncover the usable range of pH and AAH before bath maintenance is required. Optimal black nickel coating can be produced when the pH was above 5.5 and AAH was below 0.2Ah. A highly black coating can still be produced when pH was reduced to 4.5 and AAH to 0.4Ah.

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