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The process of electroplating in presence of Nickel salts

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Abstract

Electroplating process has been carried out by utilising the Watt's Bath without brighteners. Plots of weight change of electrodes versus current density shows that weight loss of anodes and weight of deposits on cathodes are proportional to current density and plating time. While plots of weight change of electrodes versus temperature shows no significant influence of temperature to weight change of electrodes. All plots are compared with theoretical values and shows excellent agreement with Faraday's Laws. Products that are produced by utilising cast nickel anodes show very good corrosion properties in normal condition, and good appearance without using brighteners.

Keywords: Electroplating, Lead anode, Iron electrode, Sulphate salt, Chloride salt.

Introduction

The electroplating process has been carried out by utilising the Watt's Bath to observe the dissolution of cast nickel anode and the deposition of metallic nickel on the iron cathode, and establish the effect of various electroplating parameters of nickel deposition.

On passing current to solution, the nickel sulphate dissociates into Ni^{2+} ion and SO_4^{2-} ion according to this reaction:

$$NiSO_4 \longrightarrow Ni^{2+} + SO_4^{2-}$$

At the same time, water itself also dissociates:

$$H_2O \longrightarrow H^+ + OH^-$$

These ions can exist independently of one another in the solution with the numbers of positive and negative charges stand equal. Under the influence of a potential, applied between two electrodes immersed in the solution, the ions will migrate in manner where the positively charged ions migrate towards the cathode or negative electrode while the negatively charged ions migrate towards the anode or positive electrode[1].

When the anode is the same metal that of the solution, the anode will dissolute to form Ni^{2+} ions and form a positively charged outer layer under an applied potential. At the cathode, the outer layer performs a negatively charged layer under the same applied potential after receiving electrons from the current supply. This attracts adjacent Ni^{2+} ions from NiSO$_4$ solution and hence deposit on the surface of cathode by withdrawing electrons. At the same time, the empty spaces left by the deposited Ni^{2+} ions in the solution is quickly replaced by the dissolute Ni^{2+} ions from the nickel anode. Due to this reason, the concentration of Ni^{2+} ions in the solution is remaining constant until the anode is completely dissolute[1]. Nickel sulphate is the principal source of nickel ions in nickel plating[2]; nickel chlorides improves anode dissolution and increases solution conductivity[3]; boric acid helps to produce smoother, more ductile deposits[4].

Material and Method

The apparatus that were arranged and used for the experiment is given in the form of diagram in Figure 1. The electrodeposition process was carried out in a 1-litre beaker where 2 nickel-plated electrodes and 1 iron electrode were used as anodes and cathode respectively.

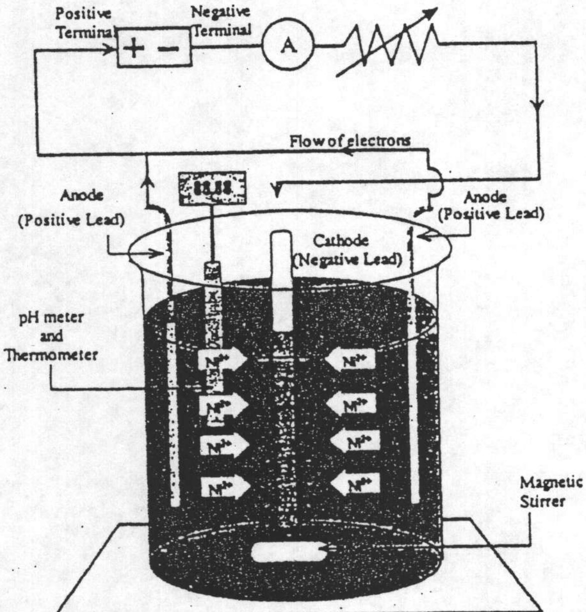

Fig. 1. Diagram of electroplating apparatus

The electrodes were first gone through the process of solvent degreasing: cold cleaning in room temperature by dipping into toluene, washing by mechanical agitation and finally wiping by cloth to remove grease and oil on the electrodes' surface.

This was followed by pickling operation in hydrochloric acid (20% in weight) for 30 seconds to remove scale, oxide and rust. The electrodes were washed with distilled water, wiped and dried[7]. The cathodes (iron electrodes) were marked 8 cm from bottom and wrapped with tape before weighing. The eight-centimetres-area was the area where the nickel deposition would take place when it was immersed into the electroplating bath. The water level of the electroplating bath was not stable due to mechanical agitation. Wrapping the cathodes prior to the electroplating process assures the electroplating area (area that exposed to electroplating bath) is always constant and hence the current density applied is constant.

The electroplating bath was prepared base on the ingredients formula of Watt's bath[8]:

300g/1 Nickel Sulphate Hexahydrate ($NiSO_4.6H_2O$)
45g/1 Nickel Chloride Hexahydrate ($NiCl_4.6H_2O$)
35g/1 Boric Acid (H_3BO_3)

In order to accomplish the objectives of performing the experiment, 3 electroplating parameters: temperature, current density and plating time, had been vary-related into two main sub-experiments

i. Experiment I: To determine the effect of various relations of current density and plating time to the weight of nickel deposit in a constant temperature condition.

ii. Experiment II: To determine the effect of different temperature to the weight of nickel deposit in constant current density and plating time.

Experiment I was started by flowing current density of 2.0 A/dm^2 for 20 minutes in constant condition that was pH 6, at 55°C. This was followed by using 2.5, 3.0, 6, 4.0, 4.5, 5.0 A/dm^2. It was repeated with the duration of 30-minutes-plating time and 40-minutes-plating time making total 21 specimens. While the Experiment II was started at the temperature of 30°C in constant condition: 6 Adm^{-2}, pH 6, followed by 40, 50, 55, 60, 70, 80°C and 100°C making 8 specimens. The reason to perform one of the electroplating processes in temperature of 100°C is to make comparison between final specimens in an extreme condition, which is high temperature. The mass of the cathodes and anodes before and after electroplating was determined by electronic balance and recorded.

Results and Discussion

Figure 1 illustrates the trends of dissolution of anodes, in various relations of current density and electroplating time. Theoretical values, which derived from Faraday's Laws, were used to compare with the experimental values. As Figure 1 shows, the dissolution of anodes increased gradually with the amount of current density applied and longer electroplating time was utilised.

Theoretically, no electroplating operation will deposit metal at a faster rate than that established by Faraday's Laws. However, accordingly what the results showed, there were obvious higher weight losses than that established by Faraday's Laws from some of the anodes, in another word, the anode efficiency was over 100%. The explanation is that nickel anodes are readily soluble in the electroplating solution; hence, some dissolution of the anode may occur due to chemical action by the electrolyte [6].

In Figure l, the weight loss of anode for electroplating time 1200 seconds at current density of 2.0 Adm^{-2}, was still less than what is stated by Faraday's Laws. However, when the electroplating time was increased to 1800 seconds and 2400 seconds, the self dissolution of the anodes were appeared more obviously. Thus, it can be said that, for longer electroplating time, the more anodes will dissolute readily.

During the electroplating process, it was found that a black, poorly conductive and adhesive film, $Ni(OH)_2$ was deposited on the anode by the chemical reactions between Ni^{2+} and the products of oxygen reduction. In the presence of oxygen, precipitation of $Ni(OH)_2$ at the anode due to increase in local pH from oxygen reduction, diminishes both nucleation and growth of nickel at cathode [10].

The deposition of cathodes trends, in various relations of current density and electroplating time, is illustrated in Figure 2. The amount (weight) of deposition of cathode, overall, involving different electroplating condition in the experiment, was proportional to the electroplating time and current density.

It is clearly shown from the plots that the trends of deposit weight on cathode could never higher than the theoretical value. Thus, unlike anodes, the efficiency of cathodes was always less than 100%. That is, part of the current applied had been wasted during the electroplating operation. The explanation is that a small percentage of the current is consumed at the cathode in discharging hydrogen ions[2].

Figure 3 shows the trend of weight changes of both cathodes and anodes under different temperature, compared with theoretical weight (derived from Faraday's Laws). The trends show that there was no obvious sign that changes in temperature directly affected the weight changes of both cathodes and anodes. However, the weight changes of both cathodes and anodes were increased, not a obvious way, when the temperature of electroplating bath was increased from 30°C to 55°C. The weight changes were then decreased slowly when the temperature increased from 60°C to 100°C.

Temperature is not a factor in influencing the weight loss of anode and weight gain of cathode according to the Faraday's Laws but it does influence the mobility of ions. Warm electroplating bath increases mobility and thus lets more metal ions diffuse in and out from electrodes into the electroplating bath and lowers the over potential. The ideal temperature of electroplating bath is ranged from 45°C to 65°C.

The electroplated samples, which were produced in low temperature (30°C and 40°C), gave dull appearances; while higher tempera-

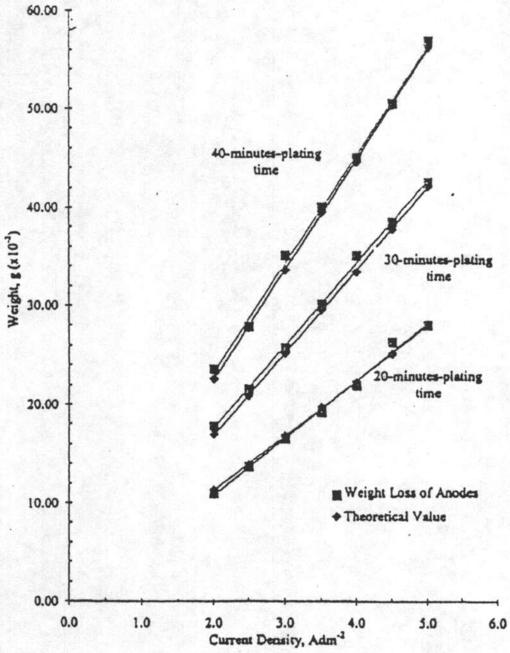

Figure 1. Plot of Weight Loss of Anodes (g) vs. Current Density (Adm^{-2})

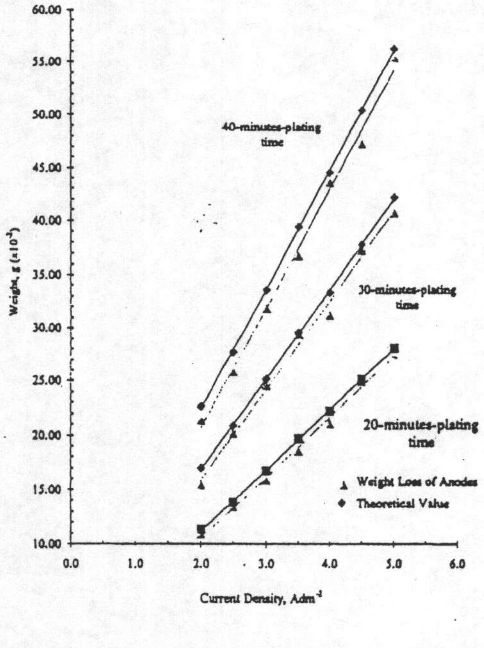

Figure 2. Plot of Deposit Weight on Cathodes (g) vs. Current Density (Adm^{-2})

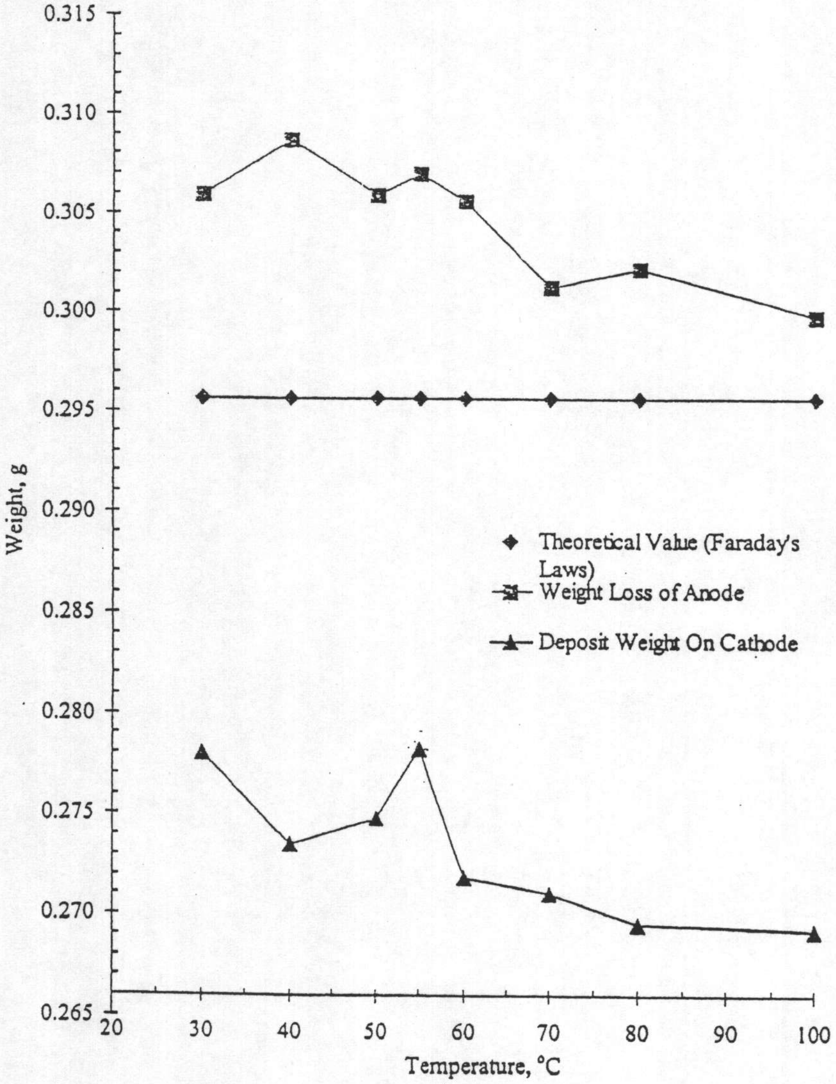

Figure 3. Plot of Weight Changes of Electrodes (g) vs. Temperature (°C): Experiment II (30-minutes-plating time)

ture (50°C to 70°C) gave bright appearances. Finally, gradually dull and brownish appearances when the temperature was increased to 100°C. Electroplating in an over high temperature that was 100°C, produced a sticky and brownish deposit but still possess acceptable corrosion resistance ability.

Agitation plays important role in producing equal and smooth surface. Unstirred bath produced products, which are unequally plated, and with spots that allow rusting especially at crevices at the surface.

The pH of electroplating bath had been changing as electroplating process proceeded. It is because small amount of H^+ ions are converted to hydrogen gas, which evolved from the cathode during the electroplating[11]. The evolution of hydrogen hence gives an excess of hydroxyl ions in the cathode layer causes the pH raises. With the increase in pH at the cathode there is the possibility that hydroxide would be precipitated on the cathode surface[6].

Hydrogen evolution in the form of hydrogen bubbles, which was occurred during the electroplating process, adhered at the surface of cathode. In unstirred electroplating bath, these bubbles grow large enough to detach of their own accord. In unstirred Watts bath, the surface pH was found to increase gradually from 4.0 - 6.5 during the first 120 s of nickel deposition[9] at 1 mAcm^{-2}. They would prevent electroplating at the site of the bubble and therefore pitting or rusting would occur.

Figure 4 and Figure 5 shows the sample, which was produced from 100°C-electroplating bath, was coated with dark brownish coloured layer that was believed an oxide. The adhesive oxide film was adhered relatively stronger than the oxide films formed on anodes. It could be removed by using sand paper. It was further discovered that a bright nickel deposit was adhered strongly at the surface of the iron electrode, under the oxide film. The same observation was also occurring on other dull electroplated cathodes. Notice that those obvious bright scratches were nickel deposit under the oxide film.

To explain these phenomena. However, it is believed that this oxide film was ferum (III) oxide, (Fe_2O_3), which was formed when the reactive ferum (cathode) react with oxygen from the solution. High electroplating bath temperature promoted higher energy for ferum and higher mobility for anion (oxygen from water) to react and hence produced darker (thicker) oxide film.

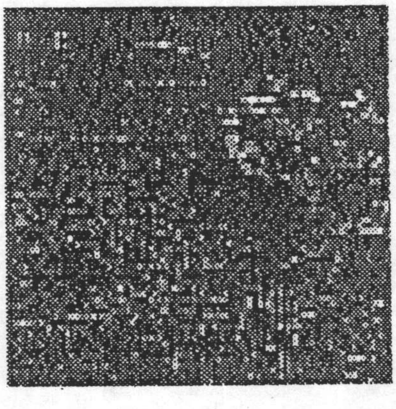

Figure 4. Microscopic photo of sample produced from Experiment II under 100°C, captured by utilising magnification of 100 X without polarised lenses.

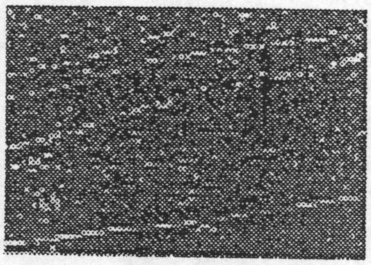

Figure 5. Microscopic photo of sample produced from Experiment II under 100°C , captured by utilising magnification of 200 X without polarised lenses.

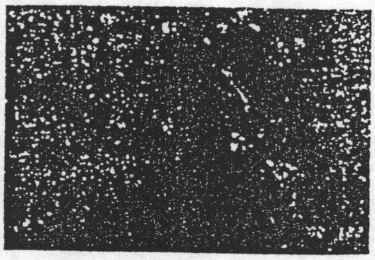

Figure 6. Microscopic photo of sample with miniature holes captured by utilising magnification of 100 X with polarised lenses.

Figure 6 and Figure 7 are the strong evidences that the bubbles of hydrogen that adherent at the surface of cathodes during electroplating operation retard the deposition of the productive nickel layer on cathodes. The small red brownish holes were the rust formed when those parts were not protected by nickel from corrosion.

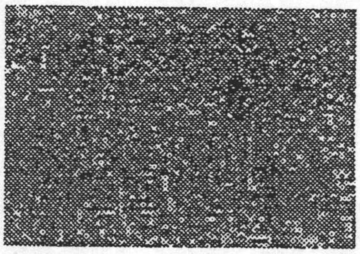

Figure 7. Microscopic photo of sample with miniature holes captured by utilising magnification of 200 X with polarised lenses.

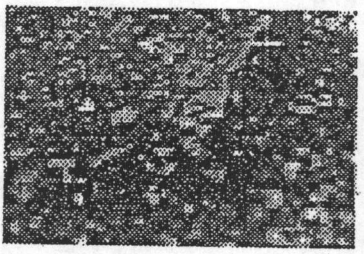

Figure 8. Microscopic photo of sample produced from Experiment I (I) captured with 200 X magnifications respectively using polarised lenses.

Figure 8 shows corrosion and rust occurred under short plating time and low current density (2.0 Adm^{-2}), the thin nickel coatings seem to be not efficient in protecting the iron electrode (cathode) from corrosion.

Conclusion

The amount (weight) of dissolution of anodes and deposition on cathodes, involving different electroplating condition in the experiment, was proportional to the electroplating time and current density. The longer the electroplating, the more weight lost from anodes; and, the more weight gained on cathodes. The results show that the electroplating operation had good agreement with Faraday's Laws.

No obvious sign shows that changes in temperature directly affected the weight changes of both cathodes and anodes. The electroplated samples, which were produced in low temperature (30°C and 40°C), gave dull appearances; while higher temperature (50°C to 70°C) gave bright appearances.

Electroplating in high temperature (100°C), produced a sticky and brownish deposit but still possess acceptable corrosion resistance ability. During the electroplating process, it was found that a black, poorly conductive and adhesive film, -$Ni(OH)_2$ was deposited on the anode by the chemical reactions between Ni^{2+} and the products of oxygen reduction.

The half reactions at cathode and anode can be written as below:

Cathodic Reaction : $Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$ (1)

Anodic Reaction : $Ni_{(s)} \longrightarrow Ni^{2+}_{(aq)} + 2e^-$ (2)

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