Characterisation of nickel deposits from nickel acetate bath

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The electrodeposition of nickel on mild steel was carried out using a nickel acetate bath. Cathodic polarisation studies were conducted, and cathodic current efficiency, throwing power and hardness of electrodeposits from the bath were all assessed. The effects of nickel chloride, and nickel acetate content in the bath, the pH and bath temperature on the above properties were analysed. The optimum conditions of bath composition and operation were established and the bath was found to be stable for the electrodeposition of nickel.

Keywords: Acetate bath, Nickel deposition, Cathodic polarisation, Throwing power, Hardness

Introduction

The use of the nickel electrodeposits is widespread, and cover the increasing of the life time of industrial, transport and service apparatus and also as decorative and functionally suitable metal coatings.¹ The selection of the electroplating bath chemistry, e.g. sulphate, chloride or sulphamate gives the required characterisations of the nickel electroplate. The quality of the nickel deposit is based on the pH value of the bath being held within narrow limits by adequate buffering.² The buffering action decreases the formation of pitting by influencing the hydrogen discharge potential on the cathode film and can avoid the precipitation of basic salts and their adsorption on the cathode surface. Nickel acetate has a high buffering capacity and when combined with boric acid, these salts greatly enhance the buffering action.³ Nickel acetate has high solubility and good stability in the pH and temperature ranges of conventional nickel plating. In the present study, the properties of nickel electroplating which has been carried out using nickel acetate based baths are analysed.

Experimental

The compositions of the plating baths are listed in Table 1. The studies were carried out at temperatures of 40 and 50°C and pH 3, 4, and 5. All the electrolytic solutions were prepared using analytical grade chemicals and deionsed water. The experiments were carried out in duplicate with mild steel specimens. The surface preparation prior to deposition was achieved by the following pretreatment conditions:

- (i) degreasing the polished mild steel specimens with trichloroethylene
- (ii) cathodic alkaline cleaning using an electrolyte solution containing 35 g L^{-1} sodium hydroxide

and 25 g L^{-1} sodium carbonate, and stainless steel counter electrode at current density 6 A dm⁻² for 2 min

- (iii) washing the specimen with running water
- (iv) dipping in 10% H₂SO₄ for 30 s
- (v) washing with running water and rinsing with distilled water.

The pH value of the bath was maintained using hydrochloric acid, acetic acid and sodium hydroxide solutions.

The cathode current efficiency (CCE) was studied using mechanically polished and cleaned mild steel panels of $5 \times 2 \cdot 5 \times 0 \cdot 1$ cm as cathodes in an electroplating assembly. High purity of $99 \cdot 5\%$ nickel plate was used as anode with operating temperatures of 40 and 50° C, and current densities ranging from 2 to 8 A dm⁻². The bath pH was also maintained at the levels of 3, 4 and 5. The cathodes were weighed accurately before and after deposition. The CCE was calculated using the equation $m_{exp}/m_{theo} \times 100$ where m_{exp} is the weight of the deposit obtained experimentally and m_{theo} is the theoretically calculated weight of the deposit determined according to Faraday's law.

The throwing power (TP) of the solution was measured using a Haring–Blum rectangular Perspex cell fitted with one perforated nickel anode between the two parallel cathodes of mild steel specimens where the ratio of the far to the near distance was 5:1. The percentage TP was calculated from Fields formula

$$\Gamma P\% = \frac{(L-M)}{(L+M-2)} \times 100$$

where L is the current distribution ratio (or) linear ratio (5:1) and M is the metal distribution ratio of the near to the far electrodes.

Potentiodynamic cathodic polarisation measurements were carried out using the PARSTAT 2273, an advanced electrochemical system. An electrolytic nickel plate was used as counter electrode and all the potentials were measured relative to a saturated calomel electrode. The reference electrode was connected to the working mild

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steel electrode via a bridge provided with a Luggin– Haber tip to avoid contamination and filled with the electrolyte solution under test. The capillary tip was placed as near as possible to the cathode surface to minimise the ohmic resistance drop.

The microhardness (HV) of the electrodeposited nickel was measured using an MH 6 Everone microhardness tester by making an intention on the specimen under a load of 50 g on the surface of the coating, with coating thickness of 35 μ m. The surface morphology of the nickel deposit was studied using a scanning electron microscope (SEM, Hitachi 3000H, Japan).

Results and discussion

Cathodic polarisation studies

Effect of bath constituents

The cathodic polarisation for the electroplating of nickel from baths A, B and C (Table 1) at the temperature of 40° C at pH 5 are shown in Fig. 1. The electrolyte solution of bath A has less cathodic polarisation than that of C (Fig. 1a and c) at all current density values. The shift of potential to the less negative values for bath A is due to the high solubility and dissociation of nickel chloride and greater abundance of free Ni²⁺ ions near the electrode surface. Also, it is noticed that the curve rises steeper for bath A than for bath C.

Figure 1*a* and *b* indicates the cathodic polarisation curves for the electrolyte solutions of baths A and B. The cathodic polarisation curve for bath B shifts to a less negative potential than that of bath A. This is because of the availability of free Ni²⁺ ions near the

Table 1 Composition of nickel acetate baths used in present work

Constituents of bath/g L ⁻¹	Bath A	Bath B	Bath C
Nickel acetate	100	150	100
Nickel chloride	30	30	
Boric acid	30	30	30
Sodium acetate	20	20	20
Sodium lauryl sulphate	0.1	0.1	0.1



2 Cathodic polarisation curves of nickel deposition for bath A at *a* pH 5, *b* pH 4 and *c* pH 3 at 40°C



3 Cathodic polarisation curves of nickel deposition for bath A at a 40°C and b 50°C at pH 5

electrode which is due to the additional amount of nickel acetate. However, the shift in the potential of polarisation curve between baths B and A is less noticeable than that of baths C and A (Fig. 1). Even though there is an increase in the free Ni^{2+} ions due to the excess amount of nickel acetate in bath B, there may be formation of some complexed species $Ni(CH_3COO)^+$, which cannot easily be reduced like free Ni^{2+} ions.

Effect of pH

The effect of pH on the cathodic polarisation curves of bath A at 40° C is depicted in Fig. 2. The decrease in the pH value of the bath shifts the cathodic polarisation curves to the less negative potential value. The reason for this is the significant decrease in the overpotential of the hydrogen evolution reaction. A similar observation for the effect of pH on cathodic polarisation curves was also noticed for gluconate and citrate baths.^{4,5}



4 Effect of nickel chloride and nickel acetate on current efficiency values in *a* bath A, *b* bath B and *c* bath C at pH 5 and 50°C at current density values from 1 to 8 A dm^{-2}

Effect of temperature

The cathodic polarisations for the electrodeposition of nickel from bath A at the temperatures of 40 and 50°C and pH 5 are shown in Fig. 3. The increase in the temperature of bath A shifts the cathodic polarisation curves to the less negative potential values and decreases the cathodic polarisation of nickel electrodeposition. This behaviour is due to the decrease in the activation overpotential of bath metal deposition and hydrogen evolution reaction.⁶ The increase in the temperature of the bath enhances the dissociation of the nickel electrolyte and increases the availability of free Ni²⁺ ions near the electrode surface as the result of increasing the diffusion rates.

Cathode current efficiency studies

The CCE studies were carried out at $1-8 \text{ A dm}^{-2}$. The CCE firstly increased with respect to current density showing a maximum value at the current density values of >4 A dm⁻². This was followed generally by a decrease in the value for higher current densities, for baths A, B and C under the experimental conditions of temperature and pH. The same trend was also observed for the deposition of nickel from aqueous gluconate baths.⁴ The change in current efficiency in respect of current density depends upon the conditions of the bath during plating. The decrease in current efficiency is due to the domination of the hydrogen evolution reaction in this regime. This process effects an increase in pH at the cathodic boundary layer which leads to the formation and precipitation of Ni(OH)₂ at the cathodic surface.^{7,8} The slow ionic diffusion in the precipitate limits the rate of transfer of ions to the electrode surface, so the nickel hydroxide hinders the nickel electrodeposition. 9,10

Effect of bath constituents

The CCE for the electroplating of nickel from baths A and C at the temperature of 50° C with pH 5 is shown in Fig. 4 for the current density values of 1-8 A dm⁻². Generally, bath A exhibits a higher value of current efficiency than that of bath C, which is irrespective of the







5 Effect of temperature on current efficiency values for bath A at a 40°C and b 50°C at pH 5 and current density values from 1 to 8 A dm⁻²

operating current density at bath pH 5 (Fig. 4a and c). This is due to the increase in nickel content in bath A by virtue of the presence of nickel chloride. This result coincides with the data from the cathodic polarisation curve (Fig. 1), where less polarisation is observed in bath A. The effect of nickel acetate on CCE for the electroplating of nickel has been studied from baths A and B at the temperature of 50°C with pH 5 for the current density values of 1–8 A dm⁻² (Fig. 4*a* and *b*). It has been observed that bath B exhibits a higher value of current efficiency than bath A, which is irrespective of the operating current density of the bath. A similar observation was also noted for nickel plating in a citrate bath.^{5,11} This is due to the increase in the nickel content in bath B through additional amounts of nickel acetate. It has also been observed from the figures that the difference in CCE values of baths A and B are not so significant in the higher current density regimes for bath pH 5, indicating that the effect of addition of excess nickel acetate in the bath has not improved CCE at the high current density regime.

Effect of pH of bath on CCE

The variation of CCE with respect to pH values 3, 4 and 5 of bath A has been studied at 40°C (Fig. 5). The CCE shows a decrease with decreasing pH value of the bath, which is irrespective of the operating current density of the bath. A similar observation is seen in the electrodeposition of nickel from acidic citrate baths.⁵ There is a decrease in the overpotential of the hydrogen evolution reaction at a low pH value which favours the easiest evolution of H₂, leading to a decrease in CCE. The result is also in agreement with the data from the cathodic polarisation curves (Fig. 2) where the decrease in cathodic polarisations with the decrease in bath pH value have been noticed, due to the lowering in the overpotential of the hydrogen evolution reaction. The stability of the nickel acetate complex is also affected at a low pH value because of the decrease in concentration of acetate ion at a low pH value. Hence, there is less buffer capacity value at a low pH value.

Effect of bath temperature on CCE

The change in CCE with the rise in the bath temperature from 40 to 50°C at pH 5 has been studied for bath A (Fig. 6). Bath A exhibits higher values of CCE at the high temperature, which is irrespective of the operating current density of the bath. This may be attributed to the adequate supply of ions to the cathode. In consequence, the quality of deposits was found to be good.¹² The rise in temperature reduces the diffusion overpotential of Ni²⁺ ions and increases the diffusion rate of the ions towards the electrode. Hence, there is an increase in the deposition rate of nickel and current efficiency value at a high temperature. The high temperature minimises the precipitation and incorporation of foreign inclusions in the deposit. The same trend has been seen in the electrodeposition of nickel from acidic gluconate baths.⁴ The effect of temperature on the cathodic polarisation curves (Fig. 3) also supports the above observation; the cathodic polarisation curve is shifted to the less negative potential values with the rise in the bath temperature.

Throwing power

The increase in cathodic polarisation has an equalising effect on the primary current distribution and therefore increases the TP.^{13,14} The increase in electrical conductivity makes an improvement in the TP value. Under some conditions, the TP values are negative. In such cases, the weight of the deposit at the far cathode is even less than predicted from the primary current distribution.

Effect of bath constituents

The TPs for the electroplating of nickel from baths A, B and C at the temperature of 50° C with pH 5 are shown in Table 2. Bath A with the nickel chloride gives a higher TP value than bath C, which is irrespective of the



7 Effect of nickel chloride on hardness values for a bath C and b bath A at pH 5 and 50°C with current density values of 4–8 A dm⁻²



8 Effect of nickel acetate on hardness values for *a* bath A and *b* bath B at pH 5 and 50°C with current density values of 4–8 A dm⁻²

experimental current densities operating in the bath at pH 5. The effect of cathodic polarisation moves the TP to the lower value for bath A (Fig. 1), but the strong effect of conductivity with the increase in nickel content of nickel chloride in bath A favours the increase in its TP value, over that of bath C. Bath B with the additional amount of nickel acetate has a smaller TP value than that of bath A, irrespective of the experimental current densities used in operating the bath (Table 2). Here, the decrease in the cathodic polarisation of bath B

Table 2 Throwing power of baths A, B and C at 50°C and pH 5

			Throwing power at current densities/A dm ⁻²				
Type of bath	Bath pH	Temperature/°C	3	4	5	6	
A	5	50	3.64	7.6	9.6	10.71	
В	5	50	3.36	2.37	3.1	2.16	
С	5	50	2.4	2.87	3.47	7.4	
А	5	40	2.77	6.4	7.5	9.1	



9 Effect of pH on hardness values for bath A at a pH 5, b pH 4 and c pH 3 at 40°C and current density values from 4 to 8 A dm⁻²

compared to that of bath A (Fig 1), has a strong effect of decreasing the TP value of bath B.

Effect of bath temperature on TP

The TPs for the electroplating of nickel from bath A at the temperatures of 40 and 50° C with pH 5 are also shown in Table 2. The effect of raising temperature of bath A from 40 to 50° C increases the TP value, which is irrespective of the experimental current density values used. A similar observation is also found in citrate baths.⁵ Even though the effect of cathodic polarisation with respect to the increase in the temperature (Fig 3) has an influence on decreasing the TP, the increase in conductivity with increasing temperature favours a shift to the larger TP value at the higher temperature.

Microhardness

Effect of bath constituents

The hardness values for electrodeposits of nickel from baths A and C at a temperature of 50°C with pH 5 are shown in Fig. 7, for current density values of 4- 8 A dm^{-2} . The hardness of the electrodeposit of bath A is higher than that of bath C. The additional amount of Ni²⁺ ions which have been furnished by the nickel chloride in bath A encourages greater deposition of nuclei possibly leading to an increase in hardness. The hardnesses of electrodeposits of nickel from baths A and B at a temperature of 50°C with pH 5 are shown in Fig. 8 for the current density values of 4-8 A dm⁻². The more Ni²⁺ ions which have been supplied by the additional amount of nickel acetate in bath B increase the deposition of more fine nuclei which may increase the hardness of the electrodeposit, as above. However, the difference in the hardnesses of electrodeposits from the two baths is not large. This may be because of the increase in the acetate complex formation in bath B which does not favour the formation of more nickel deposit.

Effect of bath pH on hardness of electrodeposit

The dependence of hardness of the electrodeposit on the pH value of bath A at 40°C is given in Fig. 9. There is a decrease in hardness of the electrodeposit with increasing bath pH values, which is irrespective of the experimental current density values of bath. The same trend was also







11 Images (SEM) of Ni electroplated from bath A at a pH 5 and b pH 4 at 50°C and c pH 5 on 40°C at current density of 4 A dm⁻²

observed in the electroplating of nickel from a citrate bath.⁵ At a low pH value, enhancement of the hydrogen evolution reaction and higher adsorption on the cathode surface and a decrease in the number of active sites of the nucleation of nickel, occur. Hence, there is a production

of coarse grain deposits characterised by low hardness values at these low pH values. The increased buffering capacity of nickel acetate in conjunction with the boric acid gives rise to smooth, fine grained deposits, and makes suitable conditions for the stabilisation of basic colloidal hydroxide at a high bath pH value with a consequent high value of electrodeposit hardness.

Effect of bath temperature on hardness of electrodeposit

The variation of hardness of the electrodeposit with the temperature of bath A has been studied at pH 5 (Fig. 10). In general, a high hardness value is due to the formation of very fine crystallites of the nickel deposit, so the grain boundaries make an essential contribution to microhardness. The increase in the temperature of bath A from 40 to 50°C, is seen to give an increase in hardness of the electrodeposit, which is irrespective of the operating conditions of current density values of the bath (4- 8 A dm^{-2}). Increasing the bath temperature favours the formation of more nuclei thereby increasing the hardness of the deposit as observed. Images (SEM) of Ni electroplated from bath A at pH 5 and 4 at 50 $^\circ\mathrm{C}$ and pH 5 at 40°C for current density of 4 A dm⁻² are shown in Fig. 11. Figure 11a consists of grains of small size with the formation of agglomerates in some places. There is formation of dendrites in Fig. 11b. The formation of small voids is seen in Fig. 11c, with is associated to a low hardness value.

Conclusions

The addition of nickel chloride to the acetate bath increases the CCE and the TP of bath and the hardness of electrodeposits. But the additional amount of nickel acetate does not give any marked change in CCE and hardness of electrodeposits, especially at the high current density regime and decreases the TP of the bath. The above parameters show a marked change when pH is varied among pH 3, 4 and 5. The bath temperature also affects the properties of bath, with higher values of current efficiency and hardness shown at a high temperature. Hence, the bath consisting of 100 g L⁻¹ nickel acetate and 30 g L⁻¹ nickel chloride, with other additives as given, operated at pH 5, temperature 50°C and medium current density of about 4–5 A dm⁻² is a good and stable regime for the electrodeposition of nickel.

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