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# Electrodeposition of catalytically active nickel powders from electrolytes of various anionic compositions

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The electrodeposition of nickel powders from different baths containing the same chemical constituents except for the anion was studied. The baths were based mainly on aqueous dilute solutions of nickel sulphate, chloride, iodide, nitrate and acetate. A detailed study was carried out to investigate the influence of these anions on the cathodic polarization curves, current efficiency, growth morphology and catalytic activity of the electrodeposited nickel powders. The characteristics tested were affected to different extents by the nature of the anion employed. X-ray diffraction studies proved that the deposited powders were very pure and had the face centered cubic structure with the orientations {111}, {200}, {220}, {222} and {311} respectively.

## 1. Introduction

Nickel powders have important industrial applications. They are commonly used in alkaline batteries, as catalysts and as pigments in anti-corrosion paints. In addition, they have found several other recent applications which depend on their magnetic properties [1, 2].

The production of electrodeposited nickel powders from different baths has been investigated by many authors [2–7]. Some authors [2–4] recommend sulphate-chloride or chloride baths for this process, but the use of such electrolytes is not always justified. This is because of the necessary corrections needed to maintain a constant electrolyte composition and the resultant large amounts of chemical reagents consumed. The use of all-sulphate baths overcomes the above-mentioned drawbacks, and in addition they give better results than sulphate-chloride baths [6]. Moreover, successful deposition of nickel powder has been reported from sulphate bath containing buffering agents [7]. Under these conditions, it was possible to produce nickel powders of definite shape, size and catalytic activity from sulphate baths by carefully controlling the bath composition. However, sulphate electrolytes possess a number of specific disadvantages. For example nickel anodes are readily passivated in these baths at comparatively low current densities and the electrical conductivity is much less than that of sulphate-chloride electrolytes [6, 7].

The electrodeposition process and the character and properties of the deposit depend to a great extent upon the nature of the anion of the salt used as electrolyte. These effects are related to the change in activity of the cation of the metal deposited, the formation of complexes between the cation and anion used [8], the capacity of the cathode for inhibition and the specific adsorption of individual anions [9]. These various effects of the anions have not been thoroughly investigated and no information is available on their effects on the electrode-position of nickel powder. Even for those systems which have been studied no correlation can be made since measurements were carried out under different experimental conditions. Therefore, a more complete understanding of the anion effects is required.

Thus, the present study was carried out to investigate the influence of various salt-anions on the electrodeposition of finely divided nickel powders in an attempt to find a bath of optimum anionic composition.

## 2. Experimental details

The electrodeposition baths used were prepared with different anionic composition within the optimum concentration range of bath composition which had previously been used for successful deposition of nickel powder from sulphate baths [7]. All chemicals used were of analytical grade (BDH). The baths were prepared in distilled water and their compositions are illustrated in Table 1. Electrolysis was carried out in a rectangular Perspex cell as outlined elsewhere [10]. Copper was used for the cathode and nickel for the anode.

For cathode polarization measurements during deposition, the cathode was electrolytically contacted to a saturated calomel electrode via a salt bridge drawn into a very thin capillary to minimize the error due to the potential drop across the electrolyte [11]. A Wenking potentioscan (Model POS 73) was used to measure the polarization curves relative to a saturated calomel electrode (SCE) and data were recorded automatically by means of a Philips X-Y recorder (Model PM 8132). The Tafel slope was calculated from a plot of cathode potential versus logarithm of the current density. The throwing number, $N$, was calculated from the slope, $b$, and the specific resistance, $\varrho$, of the electrolyte using $N = b/2\varrho$. The cathodic current efficiency ($f$%) was determined by using a standard

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*Table 1. Composition of the baths investigated*

| *Compound* | *Concentration* ($mol\,l^{-1}$) *of compound in the baths* | | | | |
|---|---|---|---|---|---|
| | *Sulphate* | *Chloride* | *Iodide* | *Nitrate* | *Acetate* |
| $NiSO_4 \cdot 6H_2O$ | 0.0125 | – | – | – | – |
| $(NH_4)_2SO_4$ | 0.23 | – | – | – | – |
| $Na_2SO_4 10H_2O$ | 0.07 | – | – | – | – |
| $NiCl_2 6H_2O$ | – | 0.0125 | – | – | – |
| $NH_4Cl$ | – | 0.23 | – | – | – |
| NaCl | – | 0.07 | – | – | – |
| $NiI_2 7H_2O$ | – | – | 0.0125 | | |
| $NH_4I$ | – | – | 0.23 | – | – |
| NaI | – | – | 0.07 | – | – |
| $Ni(NO_3)_2 6H_2O$ | – | – | | 0.0125 | – |
| $NH_4NO_3$ | – | – | – | 0.23 | – |
| $NaNO_3$ | – | – | – | 0.07 | – |
| $Ni(OOCCH_3)_2 4H_2O$ | – | – | – | – | 0.0125 |
| $CH_3COONH_4$ | – | – | – | – | 0.23 |
| $CH_3COONa\ 3H_2O$ | – | – | – | – | 0.07 |
| $H_3BO_3$ | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |

copper coulometer. X-ray diffraction studies were carried out using a Philips X-ray diffractometer (PW 1710), with nickel filter and copper radiation. The chemical analysis of the electrodeposited powders was carried out by means of an atomic absorption spectrophotometer (Perkin-Elmer Model 5000). The morphology of the as-deposited powders was examined with a scanning electron microscope (JEOL Model JSM 35). Finally, the relative catalytic activities ($D$%) of the deposited powders were tested by monitoring the decomposition of 0.4% $H_2O_2$ as a model reaction by the same method and apparatus which were described previously [10]. Unless otherwise stated all types of measurements were carried out at 25 ± 1°C using a galvanostatic method.

## 3. Results and discussion

### 3.1. *Polarization curves*

The cathodic polarization curves (Fig. 1) for the electrodeposition of nickel from the investigated baths were observed to shift to more negative values at constant current densities, when passing from one anion to another in the order $NO_3^- < SO_4^{2-} < Cl^- < I^- < C_2H_3O_2^-$. In addition, a gradual increase in the potential was observed with increasing current density. This indicates an activation-type of polarization [12, 13] and can be seen more clearly in Fig. 2 which shows approximate Tafel behaviour within the current density range 0–0.033 $A\,dm^{-2}$. At high current densities the lines became curved indicative of concentration overpotential and, in particular, diffusion overpotential. Furthermore, the change in the slopes of the Tafel relations from one bath to the other may be attributed to the codeposition of $H^+$ ions in all cases, especially at high current densities [14]. It was also observed that the Tafel slope and throwing number changed in the same previous anion order.

The observed shifting in the polarization curves may be explained in terms of the polarizabilities of the respective anions, which are present in large excess (e.g. 1.50 g ion $l^{-1}$) and their influence on the type of chemical bonding in the $Ni^{2+}$-anion complex ions formed in each bath. It was also found that the polarizabilities $P$ ($mm^2\,mol^{-1}$) of these anions (Table 2) increase in the same sequence [8] as the polarization curves shift. These results are in agreement with the values of the stability constants, log $K_1$ in the $Ni^{2+}$-anion complex ions [15] which are listed in Table 2. It was observed that increasing of polarizability and/or stability of the $Ni^{2+}$-anion complex ions decreased the activity of the free $Ni^{2+}$ ions. Such effects may be responsible for the observed shift in the polarization curves and the deposition potentials of nickel assuming more negative values. Furthermore, the pH of the as-prepared acetate bath was relatively high, consequently the high polarization observed from this bath compared with the other investigated anion baths is

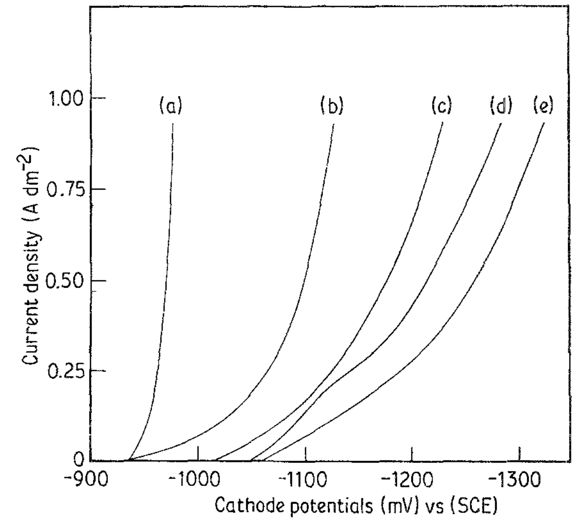

Fig. 1. Polarization curves for nickel electrodeposition from different baths: (a) nitrate; (b) sulphate; (c) chloride; (d) iodide and (e) acetate (see Table 1).

*Table 2. Some characteristics of the anions-baths investigated*

| *Property* | *Bath* | | | | |
|---|---|---|---|---|---|
| | *Nitrate* | *Sulphate* | *Chloride* | *Iodide* | *Acetate* |
| pH | 4.75 | 4.95 | 4.60 | 5.30 | 6.65 |
| Log $K_1$ (*stability constant*) | −0.22 | −0.01 | 0.07 | – | 0.83 |
| $P$ ($mm^2 mol^{-1}$) (*polarizability**) | 360 | 390 | 890 | 1910 | – |
| $E_d$ (mV) (*deposition potential*) | 948 | 1000 | 1144 | 1152 | 1170 |
| $\varrho$ ($\Omega$cm) (*resistivity*) | 37.04 | 25.64 | 34.48 | 33.33 | 52.63 |
| $b$ (*Tafel slope*) | 0.0570 | 0.0287 | 0.0297 | 0.0196 | 0.0296 |
| $N \times 10^{-4}$ (*throwing number*) | 7.69 | 5.63 | 4.30 | 2.94 | 2.81 |
| $f$(%) (*current efficiency*) | 5.39 | 7.11 | 34.93 | 21.02 | 6.92 |
| $D$(%) (*catalytic activity*) | 11 | 23 | 0 | 45 | 14 |

* The polarizability of water is 370 $mm^2 mol^{-1}$

expected. This may be attributed to the increase in the hydrogen overpotential arising from the corresponding decrease in the concentration of $H^+$ ions in the bath [16, 17].

### 3.2. *Cathodic current efficiency*

The percentage cathodic current efficiency ($f$%) of nickel powder electrodeposition was determined as a function of the anion type employed in baths 1–5. The deposition was conducted at a constant current density of 6.66 A $dm^{-2}$ for duration of 10 min and the results are given in Table 2. Generally, the cathodic current efficiency of the electrodeposited powder obtained is relatively low and this may be attributed to the high overpotentials observed for the deposition process as shown in Fig. 1 and to the expected codeposition of $H^+$ ions [14]. The effect of various anions in the cathodic current efficiency originates from their effect on the dissolution of the nickel anode and/or $Ni^{2+}$ complex ions in the bath [18].

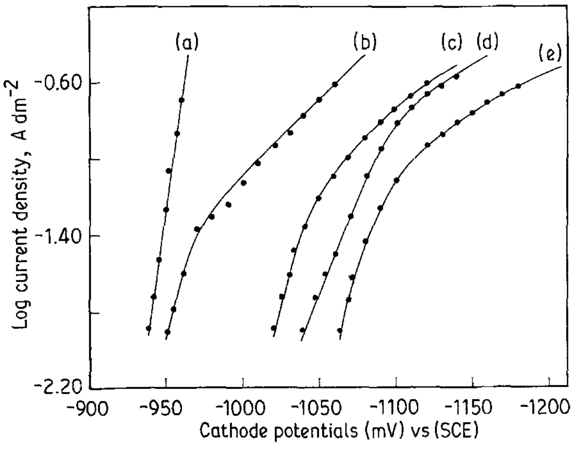

Fig. 2. Tafel lines for nickel electrodeposition from baths: (a) nitrate; (b) sulphate; (c) chloride; (d) iodide and (e) acetate.

Inspection of Table 2 shows that the $f$% obtained from these anion baths can be divided into two groups; very low, obtained from $NO_3^-$, $C_2H_3O_2^-$ and $SO_4^{2-}$ baths, and moderate obtained from $I^-$ and $Cl^-$ baths. The relatively low $f$% in the acetate bath can be attributed to the low specific conductance of the bath [7, 19] and/or the relatively high stability constant of its $Ni^{2+}$-complex ions [15]. This latter factor applies also to the $SO_4^{2-}$ anion. In addition, the passivation of the nickel anode in some baths, as in the case of $SO_4^{2-}$ and $NO_3^-$, could also account for this low $f$% [6]. The moderate $f$% obtained from $I^-$ and $Cl^-$ baths may be ascribed to the comparatively better activity of the nickel anodes in these baths [20].

### 3.3. *X-ray diffraction analysis*

X-ray studies were carried out on the electrodeposited nickel powders from the baths under test at a current density of 6.66 A $dm^{-2}$ and duration of 30 min. Table 3 shows typical data for the deposit obtained from the iodide bath. Regardless of the nature of the anion used in each bath, the data obtained revealed that nickel powders are deposited with the crystalline f.c.c. structure and exhibit the orientations {111}, {200}, {220}, {311} and {222} respectively. Moreover, the powders are deposited in a very pure form as inferred from the good agreement between the values of the calculated and the standard lattice parameters. In addition, the same behaviour was observed for powders prepared over long periods of electrolysis (3 h).

### 3.4. *Chemical analysis*

Sometimes, electrolytic powders contain contaminants such as oxides and salts of the medium [1]. Chemical analyses of the deposited powders obtained at short (0.5 h) and long (3 h) periods of electrolysis

*Table 3. X-ray diffraction data of electrodeposited nickel powder deposited from the iodide bath*

| *Line* | $2\theta$ | *d* (Å) | | $I/I_0$ | *hkl* | *a* (Å) | | |
|---|---|---|---|---|---|---|---|---|
| | | *observed* | *standard* | | | *observed* | *average* | *standard* |
| 1 | 44.5 | 2.0342 | 2.040 | 100 | (111) | 3.5233 | | |
| 2 | 51.92 | 1.7596 | 1.720 | 46 | (200) | 3.5192 | | |
| 3 | 76.74 | 1.2409 | 1.246 | 35 | (220) | 3.5098 | 3.5177 | 3.5238 |
| 4 | 93.00 | 1.0619 | 1.062 | 23 | (311) | 3.5219 | | |
| 5 | 98.80 | 1.0145 | 1.017 | 16 | (222) | 3.5143 | | |

were carried out by atomic absorption spectrophotometer. The data revealed that nickel powders were deposited in highly pure form and free from any salts of the medium, hydroxide and oxide contaminants. The percentage of nickel in all samples was close to 100%. This is in good agreement with our previous data on a sulphate bath having the same chemical composition [7].

### 3.5. *Surface morphology*

The morphology of the as-deposited nickel powders deposited from the baths investigated at a current density of $6.66\,\mathrm{A\,dm^{-2}}$ and duration of 10 min was examined by scanning electron microscopy. Fig. 3(a) shows that compact metallic nickel powders were obtained from the chloride bath. The common feature of this deposit is the existence of nodular dendritic-shaped clusters; each cluster usually contains several individual grains or crystallites. In addition, the grain size of the deposits obtained from this bath were coarser than those from any of the other baths investigated. This feature may be attributed to the comparatively better activity of the nickel anode in this bath [20], as a result, the nickel ion concentration in the bath increases. An analogous coarse deposit was reported [7] for nickel powder deposited from sulphate bath containing a high nickel ion concentration. Moreover, the degree of coverage of the substrate was not complete. This can be correlated to the greater sensitivity of the copper substrate for adsorption of the chloride anion and hence the cathode is expected to be relatively inhibited. Consequently, once a nickel nucleus of sufficient size is formed its surface is relatively clean and uninhibited compared with the surrounding copper surface so that it grows more readily, giving rise to large polycrystals more or less separated from each other [21]. In addition, it is well known that, as the growth on the cathode surface continues, the true current density decreases with time, and this, in most cases, affects powder morphology in turn.

Fig. 3(b) shows the morphology of the nickel powders from the nitrate bath. This deposit is in fern-like shapes. The change in growth morphology from the nodular-dendrite shape in the case of chloride to the fern-like shape in the case of nitrate may be attributed to the large difference in the deposition potentials of nickel in the two baths. Similar dependence of the morphology upon the deposition potentials has been reported [7, 22]. The change in morphology may also be explained in the light of the small value of the stability constant of the complex formed between the nitrate anion and $Ni^{2+}$ ions in the bath and their effects on the deposition potentials as discussed previously (Section 3.1.).

As can be seen in Fig. 3(c) and (d) the nickel powders deposited from acetate and sulphate baths, respectively, form nodular grains almost covering the whole surface. The coverage and degree of dispersion of the deposit upon the substrate as well as the decrease in the grain size increases when passing from the acetate to the sulphate anion bath. This is unexpected in the light of the high polarization observed in the case of acetate relative to sulphate and its effect on the particle size [17]. The later behaviour may be attributed to the high rate of evolution of hydrogen at the cathode as observed visually in the case of acetate.

The deposit obtained from the iodide bath was a mixture of fine nodular-dendrites and fern-like shapes (Fig. 3e). Moreover, the deposit covered the substrate to a greater degree than that from any of the other baths investigated. However; the morphology of nickel deposits from the chloride and iodide baths [(a) and (e)] reveal that the grain size tends to become finer in the iodide than in the chloride bath. This is in good agreement with the increasing deposition potential in the case of iodide (Fig. 1), which may enhance the nucleation rate and hence decrease the grain size of the deposits [21].

### 3.6. *Catalytic activity* (*D*%)

The relative catalytic activity of the nickel powders was tested by monitoring the decomposition of a 0.4% of $H_2O_2$ solution as a model reaction in a flow system. As can be seen from Table 2, the catalytic activity of the deposited powders increases in the sequence chloride < nitrate < acetate < sulphate < iodide. In general, the catalytic activity was affected considerably by the nature of the anion used but a very surprising value approaching 0% was obtained from the chloride bath. This later behaviour can be correlated to the corresponding very coarse deposit obtained from the chloride bath (Fig. 3a). However, it is expected that as the particle size increases, the active surface area decreases and the catalytic activity of the powder decreases. This finding agrees with those of other investigators [2, 23].

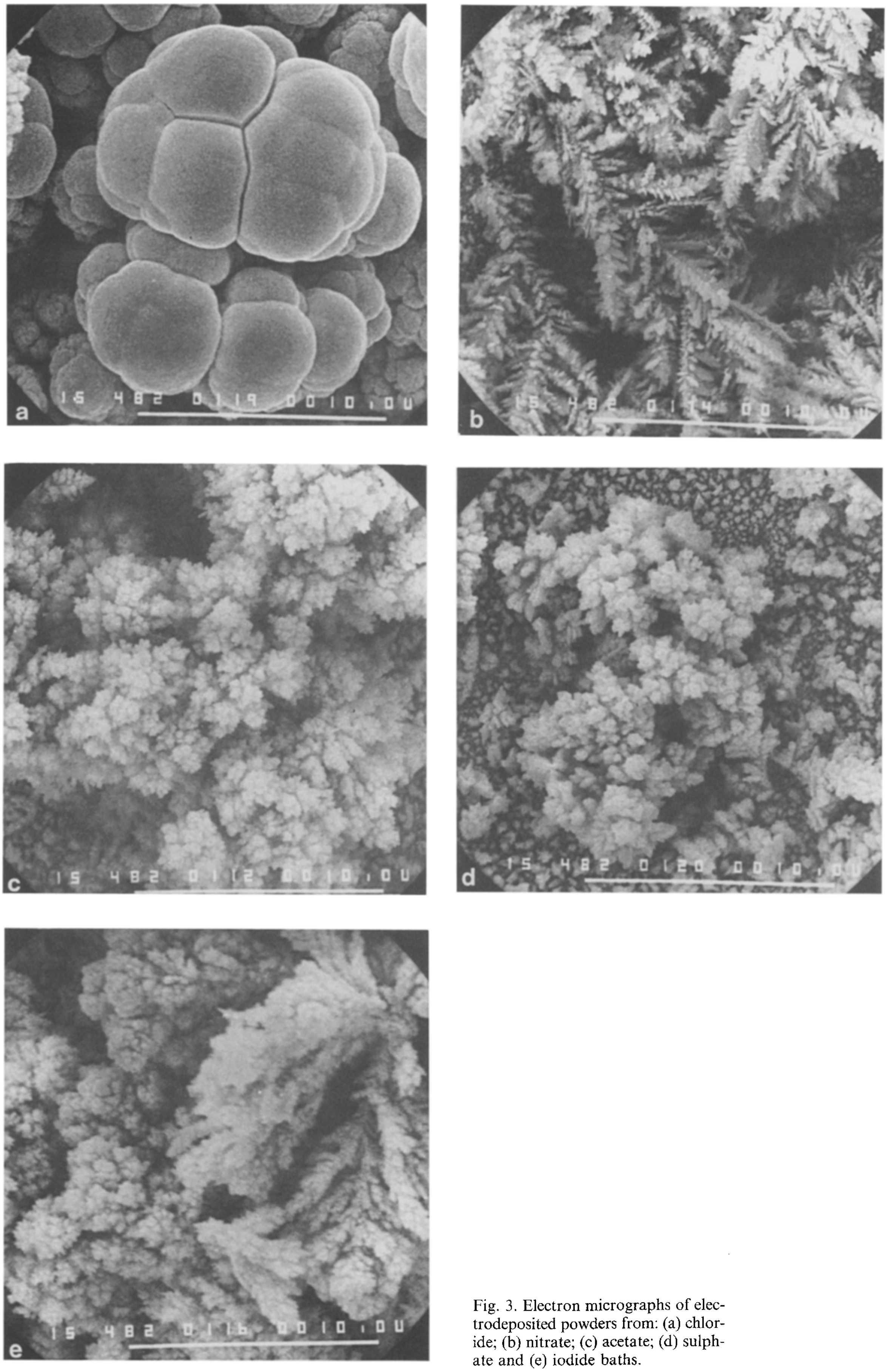

Fig. 3. Electron micrographs of electrodeposited powders from: (a) chloride; (b) nitrate; (c) acetate; (d) sulphate and (e) iodide baths.

In contrast, the catalytic activity of the nickel powders deposited from the iodide bath attains a comparatively high value (45%). This can be explained in the light of the fine grain size of the deposit obtained as shown in Fig. 3(e) and the change in the pH of the bath during deposition. The latter effect favours the formation of trace amount of basic nickel compounds. Such formation leads to an increase in the $D\%$ [1, 7, 19]. Inspection of Table 2 reveals that the catalytic activity of the deposits obtained from nitrate, acetate and sulphate was intermediate between the chloride and the iodide. This is in good agreement with the surface morphology of the deposit obtained from such baths (Fig. 3b–d) and their effects on $D\%$.

### 3.7. *Relative evaluation of the baths*

As described earlier, the electrodeposition process and the deposit characteristics were affected to different extents by the nature of the anion of the salt used in each bath. For evaluation of the best anion-bath among these tested, the cathodic current efficiency, the catalytic activity of the powders and the durability of the bath were evaluated for each case. During the electrodeposition from the chloride bath at a current density of 6.66 A dm$^{-2}$, the bath was observed to be stable for 15 min only. After this period some problems were observed; the pH of the bath increased and a dark green precipitate, which increased with deposition time, was produced in the neighbourhood of the cathode. Elementary analysis of this precipitate showed H 2.95%; Ni 41.70% and Cl 30.5%. DTA showed that the precipitate contained a hydroxyl group, while XRD did not reveal any characteristic peaks. Consequently, this precipitate was predominantly a mixture of nickel hydroxide and chloride, but the nickel deposit on the cathode was pure and free from any contaminants. Moreover, the nickel anode was easily attacked by the bath medium and had to be frequently replaced. One of the main disadvantages of the chloride bath is the lack of its catalytic activity in the resultant powder. The only advantage of this bath is the relative high $f\%$ obtained.

The electrodeposition from the iodide bath was accompanied by increasing pH of the bath, formation of a brown precipitate after 1 h. Elemental analysis, DTA and XRD revealed that this precipitate was mainly a mixture of nickel hydroxide and iodide. Moreover, the electrodeposit was pure nickel, free from any contaminant as detected by XRD.

The electrodeposition of nickel powders from nitrate, acetate and sulphate baths overcame the above drawbacks. High durability of the bath was observed in addition to the absence of any precipitate formation. However, the $f\%$ and $D\%$ were much lower except in the case of sulphate, which showed moderate $D\%$.

## 4. Conclusions

It would be possible to electro-produce nickel powders from all the baths investigated. The nature of the anion of the salt used in each bath plays an important role in the electrodeposition process and influences the characteristics of the deposit. Although the chloride bath produced a deposit with high $f\%$, the deposit was characterized by zero $D\%$ and some other drawbacks. Unfortunately, though the deposit from the iodide bath has good quality and is of high $D\%$ and moderate $f\%$ a dark brown precipitate was formed after 1 h. Nitrate, acetate and sulphate baths were characterized by more durable baths but the $f\%$ and $D\%$ were sharply reduced, except for the moderate $D\%$ of the sulphate bath. The investigated anions may be arranged in order of their favourable anionic composition as follows: $Cl^{-1} \ll NO_3^- \cong C_2H_3O_3^- < I^- < SO_4^{2-}$. Work is being pursued to further improve the iodide and sulphate baths.

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