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Activated basket anodes from nickel powder
Part I: Laboratory facilities for assessing the performance of anodes in nickel electroplating baths

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Laboratory–scale facilities have been developed for evaluating the potential performance of nickel basket anodes in an industrial electroplating circuit. Two types of electroplating baths were investigated – one for testing single anodes and the other for testing multiple anodes in small baskets under simulated industrial conditions. By the use of reference nickel anodes whose industrial performance was already known, it was established that both facilities provided an economical means of determining the electrochemical activity and current efficiencies of experimental anodes being developed for industrial use. Importantly, they also provided the means of establishing the amount of residue likely to be generated by such anodes in an industrial situation.

1. Introduction

In modern commercial nickel electroplating practice, basket anodes [1, 2] are generally employed. These anodes consist of small pieces of nickel metal, produced by a variety of proprietary processes, which are contained in titanium mesh baskets. Each basket has a solid metal base and metal hooks to allow electrical coupling to a bus-bar, and is encased in a napped polypropylene anode bag to prevent any fine particles escaping from the basket into the electrolyte and causing roughness of the electroplated surface. During continuous electroplating operations, the baskets are regularly topped up with nickel metal pieces.

Most of the present day nickel anode pieces [1, 2] are electroformed and are sulphur-depolarized, so that they dissolve uniformly in the plating-solution and leave very little anode residue or sludge. Nickel powder manufacturers would have a potential market for their product in the electroplating industry if a means could be found of producing a sintered, powder compact that was competitive with the current commercial anodes. Therefore, when a project was undertaken in the above laboratories to develop a method of producing compacted nickel powder basket-anodes for electroplating purposes, techniques had to be devised for evaluating the behaviour of individual or small batches of experimental anodes. Properties of the anodes that had to be assessed included current efficiency (C.E.), quality of cathode plate and, most importantly, the amount of anode residue.

This paper describes two electroplating facilities that were specifically designed for the purpose – one for testing single anodes, the other for simulating on a small scale the conditions obtaining in an industrial electroplating tank. The information derived from each facility and its relevance to the actual behaviour of the anodes in the industrial situation are discussed.

2. Description and mode of operation of electroplating facilities

2.1. *Electroplating bath for single anodes*

The plating-tank was a 1.5 litre Pyrex glass beaker, filled with electrolyte (see below). The electrolyte was continuously circulated by an oscillating pump through a packed bed of activated carbon at a rate sufficient to filter the total solution at least twice an hour, as required by the commercial process specifications. The total volume of solution was approximately 3 litres. Water lost by evaporation was replenished by the automatic addition of distilled water when the volume in the plating tank fell below a specified level. The plating tank, the reservoir of distilled water and the preheating tank for the circulating electrolyte were all mounted in a thermostated water-bath. In early experiments, the electrolyte in the plating-tank was stirred mechanically, but later, to more closely conform with conditions in an industrial tank, it was air-stirred. The electrolyte was maintained at 60 ± 1° C.

The anode basket was made entirely of titanium metal mesh (mesh opening, 5 mm) and measured approximately 30 mm × 40 mm × 50 mm high. The basket was spot welded to a 0.8 mm titanium metal sheet, measuring 40 mm × 55 mm. The top 15 mm of the sheet was folded into a hook enabling the basket to be hung on a copper bus-bar. An anode-bag surrounded the basket to prevent fine particles from the anode passing into the plating solution. It also provided the means of collecting and assessing the

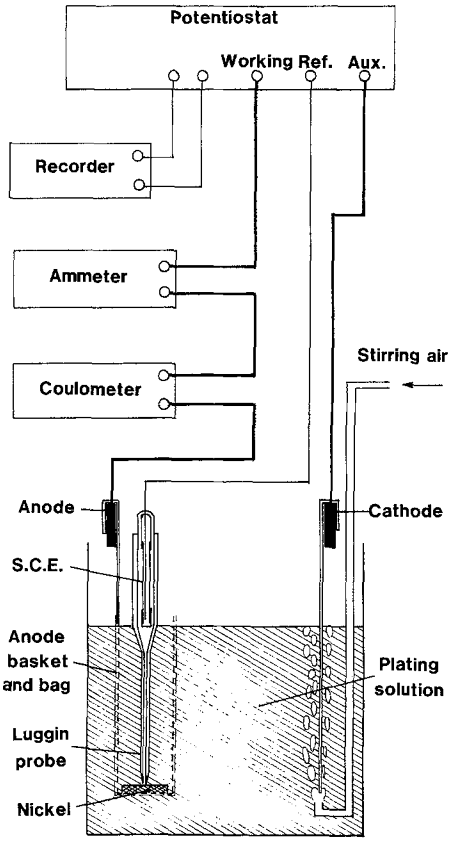

Fig. 1. Schematic diagram of the small-scale laboratory electroplating bath and monitoring system.

amount and nature of the anode residue. The cathode was a stainless steel strip, 20 mm wide, with a cathode area of 2000 mm^2 and, like the anode, hung from a copper bus-bar.

In each experiment, a single nickel anode piece was placed in the basket, immersed in the electrolyte, and anodically dissolved to extinction, or until it disintegrated with the fine particles falling through the titanium mesh into the anode-bag. Particles in the bag, which were not in contact with the basket, were no longer available for electro-dissolution.

A potentiostat/galvanostat was used to provide the electrolysis current. A constant current of 300 A m^{-2} based on cathode area (average commercial value) was applied until the potential between the anode and a saturated calomel electrode (SCE) reached a set value. The potential was then controlled at this value for the remaining period of the test. In this way, the nickel anode could be completely dissolved without any decomposition of the electrolyte occurring. The anode potential during the initial constant current period, and the current under potentiostatic control could be recorded continuously if desired (Fig. 1).

The anode and cathode current efficiencies and the percentage anode residue could be assessed from the initial weight of the anode, the quantity of charge (coulombs) passed, the weight of nickel plated on the cathode and the weight of the washed and dried residue in the anode-bag.

2.2. *Large laboratory-scale facility for simulating an industrial electroplating tank*

Two identical large laboratory-scale (LLS) electroplating tanks were constructed and run in parallel, so the following description applies equally to both baths. The tank was made from polyethylene, measured 330 mm × 330 mm and had a capacity of 16 litres of electrolyte. A March magnetic drive pump with ceramic impeller circulated the electrolyte through an industrial activated carbon cartridge filter. The electrolyte was air-stirred and its level in the tank maintained by the automatic addition of distilled water. A glass-sheathed Kanthal resistance coil for heating the plating solution was located at the bottom of the tank and the temperature of the bath was thermostatically controlled. The tank accommodated six anodes and corresponding cathodes in two rows of three pairs; the anodes were electrically isolated, but the cathodes were located on a common bus-bar. Current was supplied to each test cell (i.e., anode/cathode couple) through the rectifier and gave a nominal current density of 300 A m^{-2}. Each cell was monitored for voltage and current, which, together with the cumulative coulombs passed in each cell and the relevant temperature and time data, were recorded on a "Digistrip II" data logger. Apart from enabling the calculation of current efficiencies, the data from the unit were used to determine the required additions to the electrolyte of levellers and brighteners needed to meet commercial specifications.

Anode baskets were a scaled down version of industrial baskets. Thus, the sides and base of a basket were shaped from a continuous strip of 1 mm titanium metal sheet, 40 mm wide, with both running edges of the strip bent inwards to provide 7 mm wide flanges. Pieces of titanium mesh, each providing an open mesh area of 88 mm by 38 mm, were welded to the flanges to form the back and front of the basket. The overall height of each basket was 100 mm, the width 52 mm and the distance between front and back, 28 mm. A hook made from titanium rod was welded to either side of each basket for locating the baskets on the anode stations. Each basket was surrounded by a napped polypropylene anode-bag. Cathodes of suitable length, made from 0.8 mm stainless steel strip, 52 mm wide, were clamped to the copper bus-bars.

During the experiments, the baths were operated continuously, initially with three baskets of each type of reference nickel (see below) in each tank. The baskets were filled with nickel anodes at the start of the experiment and topped up regularly as the nickel was consumed. The initial weight of nickel in each basket and the weight of all additions were recorded. As the experiment proceeded, baskets were removed from the tanks at specified intervals and, after washing and drying, the weight of nickel remaining in the basket and the weight of fines in the anode-bag were determined.

2.3. *Industrial electroplating tank*

The electroplating tank at Siddons Industries Limited consists of a series of baths – preparative and cleaning, nickel electroplating and, finally, chromium electroplating. The nickel electroplating tank has a capacity of 15 000 l. Items to be plated (i.e., the cathode) are supported on hangers that are automatically moved along a bus-bar, which is positioned over the centre of the bath. Anode bus-bars are placed along both sides of the bath and baskets (750 mm high, 250 mm wide and 50 mm deep), containing approximately 20 kg of anode pieces, are suspended in the bath. The baskets are covered with napped polypropylene bags tied tightly to the basket hooks at the top. The baskets are regularly vibrated, manually, so that any anodes forming bridges that prevent upper level nickel moving down the basket are shaken loose, thus allowing the basket to be topped up with new anode pieces. The plating line is generally in operation seven hours per day. This procedure is followed for approximately six months before the baskets are removed for maintenance.

Power requirements for the nickel plating bath are dependent on the amount of work passing through the bath at any one time. The power supply for the line is capable of supplying 1500 A at 15 V and maintains the cathode current density at approximately 300 A m^{-2}. In the present study, two baskets, which contained different types of nickel anodes (see below), were operated in the tank, Tests were continued for a period of approximately four months; the baskets were then removed from the bath and the fines content of each bag measured.

2.4. *Anode reference material*

Two anode materials were used for testing the electroplating facilities:

(i) Commercial electroformed Inco 'S' nickel rounds (hereinafter called 'S' Ni). This nickel was sulphur depolarized and was known to give low anode residues and to perform well in industrial electroplating tanks. Each round was approximately 25 mm in diameter with flat base and irregular upper surface, giving an overall thickness of the order of 5 mm. Weights of individual rounds ranged from 14 to 20 g.

(ii) Sintered nickel powder compacts (hereinafter called 'CP' Ni). Such compacts were known to give high anode residues. Half a tonne of compacts was prepared commercially from Western Mining Corporation Ltd. nickel powder that had been heat-treated prior to compaction to avoid excessive swelling of the compacts during sintering [3]. Each compact was 26 mm in diameter, approximately 4 mm thick and weighted about 20 g.

2.5. *Plating solutions*

Industrially, bright nickel is generally electrodeposited from a standard Watts electrolyte [2, 4] containing suitable additions of brighteners and levellers (bright Watts bath). Consequently, at the commencement of the study, both laboratory-scale electroplating facilities were operated with this type of electrolyte (Udylite 913). In addition, nickel anodes are used in the plating of nickel/iron alloys. For example, Udylite have developed the "Niron" process which is marketed by the Occidental Chemical Company Pty Ltd. In this process, a propriety electrolyte (NIRON 'H') is used with nickel and iron anodes contained in separate anode baskets. Company specifications imply that the behaviour of nickel anodes in this electrolyte is similar to that in bright Watts electrolyte. Nevertheless, the behaviour of single anodes in the small laboratory electroplating facility was monitored in both Niron and bright Watts electrolyte.

2.6. *Calculations*

At the end of each test, the weight of the washed and dried fines from the anode bag was calculated as a percentage of the total nickel anode weight (i.e., nickel consumed) to give the percentage anode residue.

Anode and cathode current efficiencies for laboratory-scale tests were determined by calculating the weight of nickel dissolved or electrodeposited, respectively, as a percentage of the weight of nickel that theoretically should have been dissolved or electrodeposited by the quantity of charge that had been passed during the test.

3. Results and discussion

The industrial trial extended over four months during which the electroplating tank operated for a total of 636 h and resulted in the dissolution of approximately 50 kg of each type of anode. The two LLS plating tanks were operated continuously, one for 516 h, the other for 900 h with the dissolution of 2–2.5 and 3–3.5 kg of each type of nickel, respectively. Single anodes required 30–55 h for complete anodic dissolution. In all cases, the resulting nickel or niron electroplate was of high quality.

Table 1 gives values for anode residues and current efficiencies for both types of reference nickel anodically dissolved in the industrial tank and in the two LLS baths after 636 h operation. It also includes data corresponding to maximum percentage anode residue for 'CP' nickel in the LLS baths and gives the average values for a number of single anode pieces of each type of material dissolved in both bright Watts and Niron electrolyte. Table 2 details the data for the LLS baths, while Fig. 2 shows the weight of nickel progressively consumed in the industrial tank and the two LLS electroplating baths as measured by the cumulative weight of nickel added to each basket. Figure 3 presents typical plots of anode potential (against SCE) against plating time for single anodes of each type of reference material.

From these data the following observations can be made:

Table 1. Electroplating data generated in different plating circuits

(a) 'S' Ni anodes

Scale	*Electrolyte*	*Plating time (h)*	*Anode residue (%)*	*Current efficiency (%)*	
				anode	*cathode*
Industrial	Niron	636	0.2	NA	NA
LLS.1	B. Watts	636*	0.4	94	85
LLS.2	B. Watts	636*	~0.2	93	87
Single compacts	B. Watts	30–50	0.6 (0.2)	99 (1.5)	92 (3.5)
Single compacts	Niron	30–50	0.2 (0.2)	101 (0.6)	86 (7.1)

(b) 'CP' Ni anodes

Scale	*Electrolyte*	*Plating time (h)*	*Anode residue (%)*	*Current efficiency (%)*	
				anode	*cathode*
Industrial	Niron	636	5.3	NA	NA
LLS.1	B. Watts	250	6.5	92	86
		636*	3.6	92	100
LLS.2	B. Watts	96	5.0	97	94
		636*	~2.1	94	106
Single compacts	B. Watts	30–50	4.5 (1.2)	98 (1.9)	91 (4.7)
Single compacts	Niron	30–50	4.7 (1.1)	101 (0.5)	92 (1.0)

Notes:
NA – not available.
* – data for 636 h obtained by interpolation or extrapolation of accumulative data.
Single compact data are the averages in each case of data from 4 to 10 compacts; figure in brackets is the standard deviation for each set.

– Both laboratory-scale facilities give a clear indication of the likely industrial performance of nickel anodes with regard to the generation of anode fines.
– The laboratory-scale facilities provide additional information concerning anode behaviour that cannot be deduced from a full-scale industrial trial.

It is evident from Table 2 that, for 'CP' nickel anodes in the LLS baths, the percentage anode residues peak at relatively high values and then decrease over longer plating periods. The results imply that anode residue only continues to build up in the anode-bag until it makes good electrical contact with the base of the anode basket and an equilibrium is achieved between the rate of formation of anode fines and their rate of dissolution. Further, the difference in the anode residues for the two baths indicate that the mode of anodic dissolution and so the generation of fines is somewhat sensitive to minor variation in bath conditions; the actual cause of the difference in the present case was not determined.

Again, the curves in Figs. 2 and 3 show that the laboratory-scale facilities can provide information concerning the relative dissolution rates and electrochemical activities of anodes that is not available from

Table 2. Summary of electroplating data from the large laboratory-scale baths for 'CP' nickel and 'S' nickel anodes in bright watts electrolyte

Time (h)	*Megacoulombs*		*Anode CE (%)*		*Cathode CE (%)*		*Anode residue (%)*	
	'CP'	*'S'*	*'CP'*	*'S'*	*'CP'*	*'S'*	*'CP'*	*'S'*
Bath 1								
240	3.8	4.4	93	97	90	93	5.3	0.5
250	4.1	4.8	91	98	86	93	6.7	0.6
250	4.2	4.7	92	101	86	89	6.3	0.4
348	4.7	6.0	99	94	113	98	4.3	0.8
500	6.6	9.1	94	89	104	84	4.2	0.5
900	10.5	12.0	91	96	90	83	2.9	0.2
Bath 2								
96	1.7	1.9	97	96	94	93	5.0	0.3
192	3.6	4.1	96	96	108	71	4.6	0.2
250	4.8	6.0	92	94	101	82	4.0	0.3
516	7.1	8.7	94	93	106	85	2.5	0.3

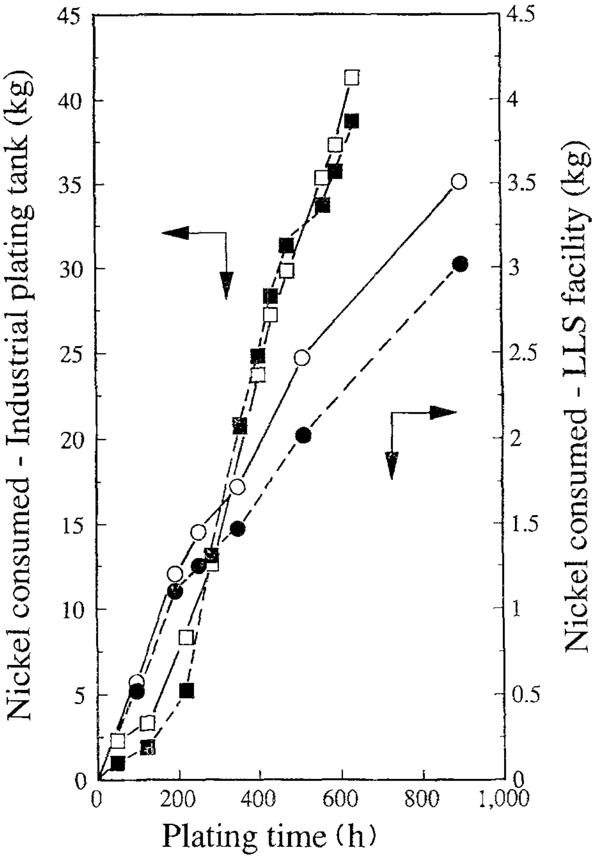

Fig. 2. Weight of nickel consumed versus plating time. (□) 'S' Ni and (■) 'CP' Ni, in the industrial electroplating tank; (○) 'S' Ni and (●) 'CP' Ni, in LLS facility (data for baths nos 1 + 2 combined).

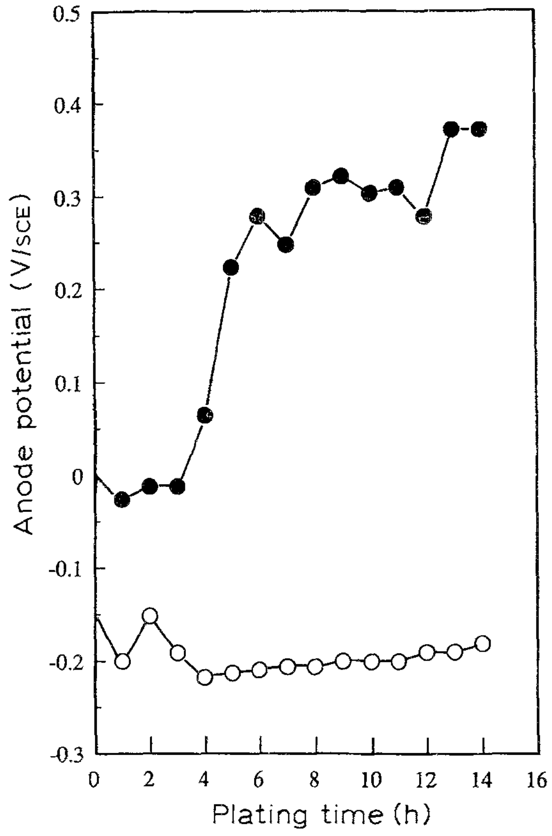

Fig. 3. Typical plots of anode potential (V/SCE) against plating time for singles anodes of 'S' nickel (○) and 'CP' nickel (●).

an industrial trial. This information can be supplemented by examining current efficiencies (Table 2), which can be determined at any stage of a plating regime. The anode current efficiencies give a direct measure of anode performance and the curves in Fig. 3 a direct measure of the electrochemical activity of single anodes of each type during electrochemical dissolution. But, because baskets of the two reference anodes in the LLS facility were tested in the same electroplating bath with corresponding cathodes mounted on a common bus-bar, the cathode current efficiencies for the individual electrode pairs cannot be considered in isolation. Nevertheless, when coupled with the above observations, the cathode current efficiencies throw further light on anode behaviour.

The power supply to the LLS facility is unregulated (consistent with industrial practice) so the current drawn is proportional to the overall internal cell resistance and, as the electrolyte and cathode assemblages are essentially common, any difference in charge passed through each anode/cathode couple can be attributed to differences in performance of the anode pieces/basket assemblages. Further, in the absence of cell partitions between anode/cathode couples in an electrolyte with good throwing power, discharge of ions will tend to occur uniformly across all the cathodes in the bath. This can result in some cathodes exhibiting abnormally high cathode current efficiences, with others in the bath registering correspondingly low values.

When two types of anode materials are being operated simultaneously in the bath, the various permutations of anode/cathode current efficiency values may lead to specific conclusions regarding the performances of the anodes in an industrial situation. For instance:

(i) If similar quantities of charge are passed through both anodes, but a relatively low anode current efficiency for one type of anode material is coupled with a high cathode current efficiency (possibly more than 100%) it can be suspected that, with that type of anode, unwanted side reactions (e.g., discharge of oxygen or chlorine) are occurring at the anode and that cathodic deposition of nickel may be faster than anodic dissolution; the use of such anodes is likely to result in the depletion of nickel ions in the electrolyte.

(ii) If the quantity of charge passed and the anode current efficiencies for the two materials are similar, but one (or both) of the corresponding cathode current efficiencies is relatively low, then side reactions (e.g., the discharge of hydrogen) may be occurring at the cathode(s) registering the low current efficiency. Anode/cathode couples with a significantly lower cathode than anode current efficiency will produce a build up of nickel in solution.

(iii) If the anode current efficiencies of the two materials are similar, but the amount of charge passed at one anode is significantly lower than at the other then, because of the tendency for current to be discharged uniformly across the cathodes, the anode passing the lesser amount of current is likely to be coupled with the cathode exhibiting the higher current efficiency (cathode C.E. possibly more than 100%). Such an outcome implies that the resistance of the anode material/basket assemblage of the anode passing the lesser charge is higher than that of the other anode.

The latter scenario applies to the anode materials used in the present study, with the 'CP' nickel/basket assemblage passing significantly less charge than did the 'S' nickel/basket assemblage. The anode potentials (versus SCE) measured during dissolution of the single anodes (Fig. 3) confirm that the 'CP' nickel is less active than the 'S' nickel. In keeping with these findings, Fig. 2 shows that in the LLS baths 'CP' nickel was consumed more slowly than was 'S' nickel. The fact that this difference in consumption rate is not evident from the industrial trial plots (Fig. 2) may mean that the difference in performance of the two anode materials is accentuated by a less satisfactory geometric aspect ratio of basket to anode pieces for the miniature baskets used in the LLS trials compared with that for the baskets used in the industrial situation. More probably, temporary bridging of the 'S' nickel anodes occurred at about 250 h plating time in industrial basket, which prevented the anodes moving down the basket; this bridging was not broken until about 500 h (Fig. 2).

It should be noted that an anode current efficiency in excess of 100% is attributed to some chemical dissolution of the anode. This is particularly so for anodes tested in niron electrolyte as the iron component of the anodes dissolves in the solution more readily than does the nickel.

4. Conclusions

The anodic dissolution of single anode pieces can provide a relatively rapid and cheap method for the preliminary assessment of the properties of basket anodes, particularly with regard to the generation of anode fines and the relative activities of anode materials during electrodissolution. Additional information can be obtained from the dissolution of multiple anodes in a large laboratory-scale electroplating facility where conditions simulate those obtaining in an industrial electroplating plant. Indeed, tests in such a laboratory facility can be monitored more closely, in more detail and, as the quantities of anodes needed for the tests are much smaller, at considerably less expense than can tests that involve the insertion of baskets of anodes in an industrial tank operating under commercial conditions.

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