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Activated basket anodes from nickel powder
Part III: Electrochemical behaviour of sulphur activated anodes

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The characteristics of anodic dissolution of nickel electroplating anodes produced from compacted nickel powder by a liquid phase sintering process have been determined. Sulphur incorporated in the sintered product was found to increase the electrodissolution activity and inhibit passivation. The activity of the anodes increased with increase in sulphur content and approached that of commerical sulphur-depolarized anodes produced by electroforming. Sintering temperature and rate of cooling during preparation of the anodes had little influence on the dissolution activity and resistance to passivation. No direct relationship was found between activity and the generation of anode fines. The rate of anodic dissolution of sulphur-containing anodes has been found to be comparable to that for synthetic heazlewoodite (Ni_3S_2 electrodes). The influence of the presence of sulphur on the kinetics of nickel dissolution is interpreted in terms of the development on the metal surface of Ni_3S_2 from which nickel is extracted to leave a sulphide of lower nickel content; the latter sulphide then reacts with underlying elemental nickel to reform Ni_3S_2.

1. Introduction

Part II of this series of papers [1] described the development of a process for the preparation from nickel powder of sulphur-depolarized basket anodes for electroplating. This liquid-phase sintering, 'LPS', process involves sulphidizing the surface of preheated nickel powder particles, cold compacting the resultant material, and sintering the green compacts in a hydrogen-containing atmosphere at 960° C. The compacts are finally cooled slowly in the sintering atmosphere.

In a parallel Japanese process [2], compacts prepared from nickel powder are sintered at a temperature above 1050° C and then quenched in water or oil. As discussed previously [1], the two processes for producing basket anodes from nickel powder are quite distinct and it is imperative to adhere to the specified sintering temperature/cooling specifications in each case if the performance of the product anodes with regard to the generation of anode fines is to be acceptable.

In both these processes, the sulphidization step results in the formation of a liquid phase at the interfaces between particles during the sintering step. As sintering proceeds, the amount of liquid in the grain boundaries and interstices of the compacts decreases, because sulphur is removed by reaction with the sintering atmosphere to form hydrogen sulphide. The concentration of sulphur in the sintered compacts depends on the level of sulphur in the green compacts, the hydrogen fugacity and flow-rate of the sintering atmosphere, the temperature and period of sintering, and the mode of cooling of the sintered compacts.

It is well established [3–7] that the presence of sulphur improves the performance of nickel anodes through inhibiting passivation. It was not known, however, whether sulphur incorporated during liquid phase sintering of compacted powders is as effective as sulphur incorporated during an electroforming process. Nor was any information available concerning the relative activities of anodes formed by the two liquid phase sintering processes outlined above.

This paper presents the results of an investigation of the current-potential relationships of anodes prepared by the sintering processes. The anode activity is compared with that found for sulphur-depolarized electroformed basket anodes commonly used in commerical nickel plating practice. An interpretation of the role of sulphur in the dissolution process is presented.

2. Experimental details

The methods used to prepare sintered nickel anodes are described in Part II [1].

Current-potential relationships of the nickel anodes were determined with electrodes prepared by attaching 1 cm diameter discs machined from the anodes to a brass rod with conducting epoxy cement (ACME E-Solder), and encapsulating in epoxy resin (Araldite D). The brass rod was tapped to fit the threaded spindle of a Beckman variable speed rotating electrode system. The epoxy was cut back to expose the metal surface.

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model 0151A sweep generator was used to control the potential and currents were recorded on a Yew type 3086 X–Y recorder. Potentials were measured against a saturated calomel electrode (SCE) and converted to the standard hydrogen electrode (SHE) scale assuming the SCE has a potential of 0.245 V with respect to the SHE [8].

A nickel sulphide (Ni_3S_2) electrode was prepared in a similar manner from a nickel compact that had been treated in a 4 : 1 H_2/H_2S atmosphere at 380° C to sulphidize a layer 2 mm thick on the surface. X-ray diffraction analysis confirmed that the surface layer had the heazlewoodite structure. A 7 mm × 8 mm block was cut from the compact and mounted so that the sulphide constituted the exposed surface in the completed electrode.

Dissolution studies on the nickel electrodes were carried out at 21° C in a nickel sulphate solution (325 g dm^{-3} $NiSO_4 \cdot 7H_2O$; pH adjusted to 4.0 with H_2SO_4) and at 60° C in a Watts solution (290 g dm^{-3} $NiSO_4 \cdot 7H_2O$; 45 g dm^{-3} $NiCl_2 \cdot 6H_2O$; 35 g dm^{-3} H_3BO_3; pH 4.5). The solutions were de-oxygenated with purified nitrogen. Fresh surfaces were generated on the electrodes before each run by abrading the surface on grade P 100 silicon carbide paper. Current-potential curves were recorded for positive-going scans at 10 mV s^{-1} commencing at the open circuit potential. The electrode was rotated at 10 Hz in order to ensure that the solution composition at the electrode surface was maintained the same as that in the bulk electrolyte.

The behaviour of nickel sulphide was also studied in the nickel sulphate solution. For these studies, a fresh surface was created by abrasion under a nitrogen atmosphere. The electrode was then transferred to the electrochemical cell without exposure to air to avoid oxidation to the electrochemical experiments being carried out.

3. Results and discussion

3.1. *Nickel in sulphate solution*

Current-potential curves were recorded for sintered nickel anodes of different sulphur content, and for an electrode prepared from a sulphur depolarized, electroformed anode (an INCO "S-round" containing 362 p.p.m. sulphur). During the first few repeated positive-going scans following the formation of a fresh surface, the dissolution activity, i.e., the current at a particular potential, increased. After about ten scans for the sintered anodes, and five for the electroformed anode, the current-potential curves did not change between consecutive scans. The potential dependence of the anodic current for the electrodes at this constant condition are shown in Fig. 1.

It can be seen from Fig. 1 that, in the low potential region, the current follows a Tafel relationship with a slope of about 110 mV. This behaviour is in agreement with previous studies [9] of the kinetics of the anodic dissolution of nickel in sulphuric acid solutions in which a 120 mV Tafel slope was interpreted in terms of a mechanism of dissolution involving the intermediate formation of $NiOH_{ads}$ and $NiOH^+$ species.

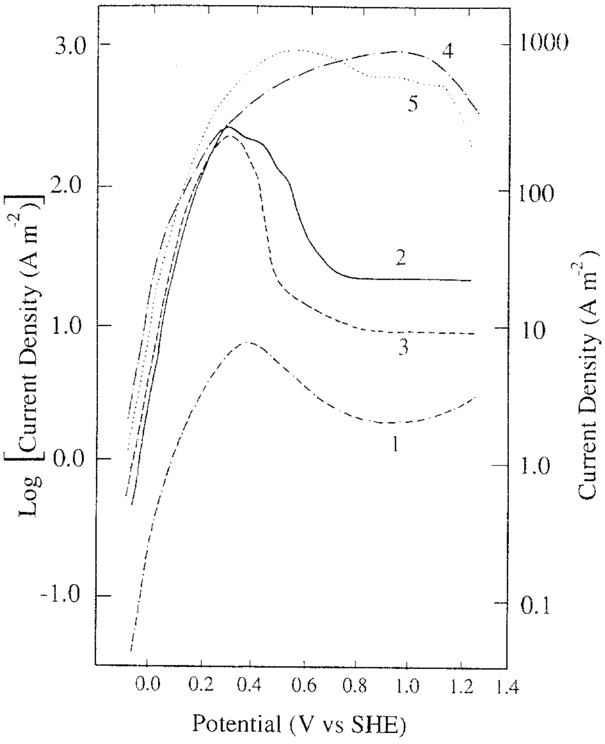

Fig. 1. Dependence of anodic current density on potential for curves 1–4 sintered nickel anodes with sulphur content: (1) 34 p.p.m. (no sulphur treatment); (2) 350 p.p.m.; (3) 633 p.p.m.; (4) 1700 p.p.m.; and (5) electroformed with 362 p.p.m., in nickel sulphate medium at 21° C. Linear potential sweeps from open circuit potential at 10 mV s^{-1}.

The data presented in Fig. 1 also show that the sintered compacts containing sulphur are much more active than the electrode prepared from nickel powder without sulphur treatment. Thus, sulphur incorporated during liquid phase sintering of compacted powders behaves in the same manner as sulphur incoporated during an electroforming process.

Marcus and co-workers [5, 10] found that, with nickel electrodes containing sulphur, the sulphur accumulates at the surface to form a layer ten atoms thick. Since the activity increases with increase in sulphur content, such accumulation would account for the increase in activity observed here for electrodes in the initial stages of anodization, although roughening of the surface as nickel is dissolved could also play a significant role. Figure 1 shows that the current at each potential for the sintered anodes increases with increase in the sulphur content of the compacts. A similar relationship has been reported [7, 11] for the corrosion of nickel in acid solution. Baer and Danielson [7] found the corrosion rate to vary with the surface sulphur coverage whereas Marshall and Jones [11] found it to relate to differences in surface roughness.

The electroformed anode (Fig. 1) displays an activity greater than that of sintered anodes of similar sulphur content. A constant current-potential curve for the former anode was reached with fewer scans than that for the latter and this is not consistent with the

Table 1. Properties of compacts used in the electrochemical experiments of Fig. 2

Property	*Sintering temperature and mode of cooling*			
	960° C		*1100° C*	
	slow cooled (A_1)	*quenched* (A_2)	*slow cooled* (B_1)	*quenched* (B_2)
Density (% that of Ni crystal)	81.7	82.1	82.2	82.0
Volume expansion on sintering (%)	4.9	4.5	4.0	4.5
Total sulphur (p.p.m.)	381	637	693	717
Sulphur in excess of equilibrium solubility limit (p.p.m.)	181	437	343	367

difference in behaviour being due to difference in surface roughness. Thus, it would appear that the sulphur is more evenly distributed in the electroformed anode and that the surface is more evenly coated with sulphur. It should be noted that the resultant higher activity observed for the electroformed over the sintered anode of equal sulphur content is equivalent to only a 0.05 V decrease in cell potential in a plating process.

It is well established that, in addition to enhancing activity, the presence of sulphur suppresses the passivation of nickel from oxide formation [3–7]. The results in Fig. 1 are also in accordance with this conclusion. Again, the effect of sulphur in the sintered anodes increases with increase in sulphur content. As before, the difference between the behaviour of the electroformed and sintered anodes of similar sulphur content is not significant in terms of nickel plating.

In the Japanese patented process [2], anodes are quenched following sintering because this procedure was considered to give rise to improved performance in electroplating. In Part II [1], it was shown that the residue produced during electroplating was much lower when the compact was quenched (0.4%) than when slow-cooled (4.9%), if the sintering temperature was 1100° C, which was within the range (1050–1400° C) specified in the Japanese patent. However, for the sintering temperature favoured by CSIRO (960° C) the residue when the compact was quenched (1.1%) was higher than when slow-cooled (0.5%). Thus, the quantity of residue formed depends critically on the formation procedure. To ascertain if the difference between the sintering temperature and mode of cooling also affects electrochemical activity and resistance to passivity, the current-potential behaviour was determined for anodes prepared under the different production regimes. The results are shown in Fig. 2; the physical properties of the anodes used in this study are presented in Table 1.

The data in Fig. 2 suggest no major dependence of performance on mode of anode formation, since the differences that do exist can largely be accounted for by the variation in sulphur content (compare curves in Fig. 2 with those for similar sulphur content in Fig. 1). Thus, it appears that the activity and the resistance to passivation of the compacted anodes depend only on sulphur concentration and distribution.

There is no apparent relationship between the quantity of residue remaining after electro-dissolution and anode activity or resistance to passivation. This is not unexpected since the residue level and the electrochemical parameters depend on the presence of sulphur in different ways. The former is determined by the quantity and distribution of sulphur in the treated powder, and by the influence of this sulphur on

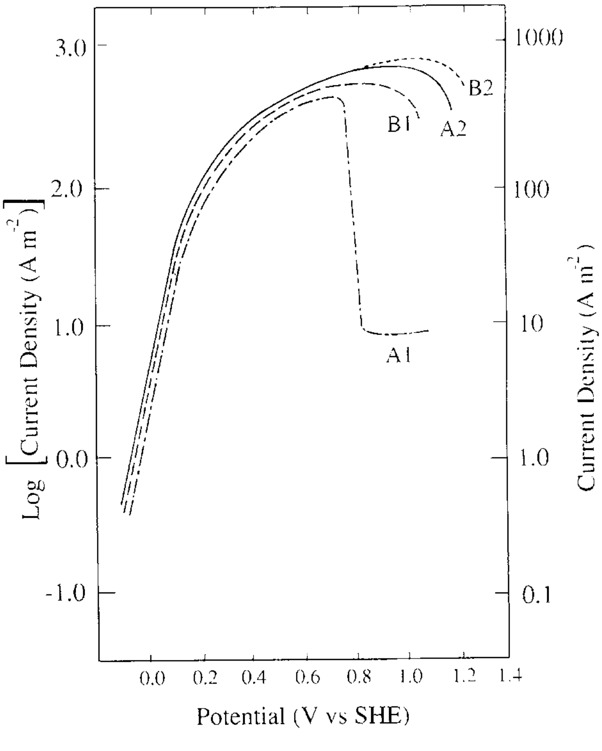

Fig. 2. Dependence of anodic current density on potential for sintered nickel anodes in sulphate medium at 21° C: (A) sintered at 960° C; (A1) slow cooled in sintering atmosphere, (A2) quenched: (B) sintered at 1100° C; (B1) slow cooled in sintering atmosphere, (B2) quenched. Linear potential sweeps from open circuit potential at 10 mV s^{-1}.

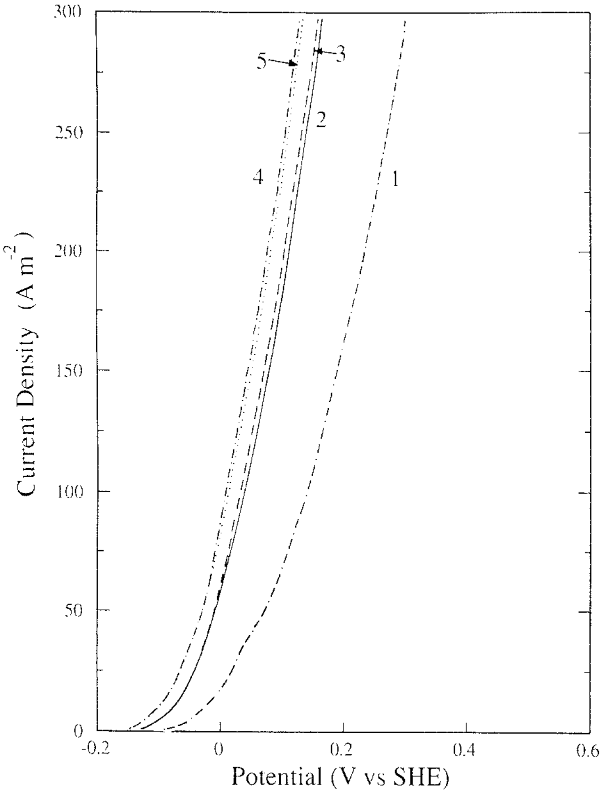

Fig. 3. Dependence of anodic current density on potential for curves 1–4 sintered nickel anodes with sulphur content: (1) 34 p.p.m. (no sulphur treatment); (2) 350 p.p.m.; (3) 633 p.p.m.; (4) 1700 p.p.m.; and (5) electroformed with 362 p.p.m., in Watts bath at 60° C. Linear potential sweeps from open circuit potential at 10 mV s^{-1}.

sintering characteristics. Most of the sulphur is removed during the sintering stage of the anode production process and the final level can vary widely for similar residues. On the other hand, the final level determines the electrochemical parameters.

3.2. *Nickel in Watts solution*

A high percentage of nickel electroplating is carried out in Watts-type solutions. Figure 3 shows the behaviour of sintered anodes and an electroformed anode in such a medium at 60° C in the current density range used in practice. Nickel passivation does not occur in the presence of chloride and hence all the anodes, including that containing no added sulphur, remain active throughout the potential range. It can be seen from Fig. 3 that the presence of sulphur enhances the rate of dissolution of nickel and that the activity increases with increase in sulphur content, as was found in the sulphate medium. Again, the electroformed anode (362 p.p.m. S) displays an activity slightly greater than that of sintered anodes of similar sulphur content. However, as with the sulphate bath, the difference is not significant as it only constitutes an increase of about 0.03 V in cell voltage during electroplating.

It has been reported [6] that S-rounds dissolve at a potential 0.4 V below that of "ordinary electrolytic nickel". It can be seen from Fig. 3 that the difference in potential at which the most active anode and that prepared without added sulphur give rise to equal dissolution currents is only 0.10–0.16 V, depending on current density. This difference between reported and observed behaviour could be due to the presence of 10 p.p.m. residual sulphur in the powder used to prepare the sintered anodes.

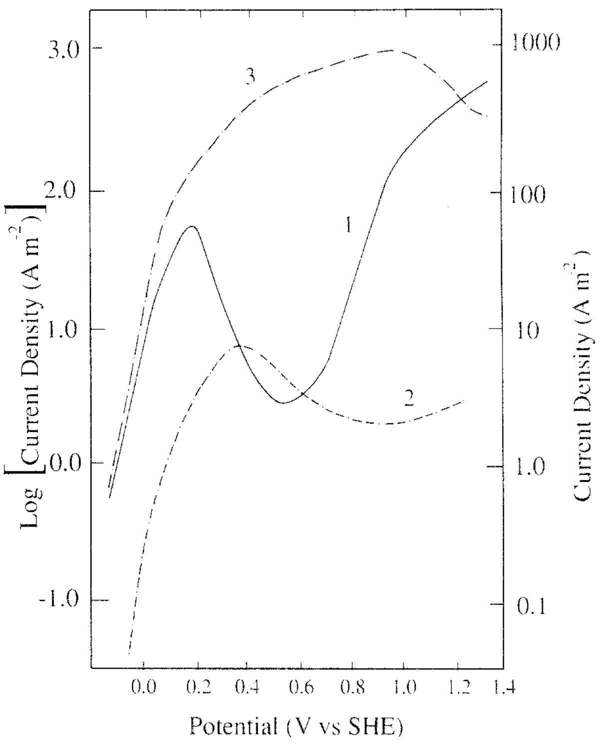

Fig. 4. Dependence of anodic current density on potential for curves 1 Ni_3S_2 and curves 2 and 3 sintered nickel anodes with sulphur content (2) 34 p.p.m. (no sulphur treatment); (3) 1700 p.p.m.; in nickel sulphate medium at 21° C. Linear potential sweeps from open-circuit potential at 10 mV s^{-1}.

3.3. *Nickel sulphide in sulphate solution*

The sulphur layer formed on nickel-sulphur alloys during anodic dissolution has been identified by X-ray photoelectron spectroscopy as Ni_3S_2 [10]. A nickel electrode coated with a 50 nm layer of Ni_3S_2 has been shown [5] to give rise to a dissolution current similar to that of nickel containing sulphur, until a potential was reached at which the sulphide layer separated from the underlying metal. Later electron spectroscopic work [7] confirmed that the sulphur layer was present as a sulphide. However, a detailed mechanism for the role of sulphur in activating nickel has not been presented.

Figure 4 shows a current potential curve for a Ni_3S_2 electrode. The sulphide layer on this electrode was sufficiently thick ($\sim$ 2 mm) for the underlying nickel to have no influence on the electrochemical characteristics. The observed behaviour can be explained in terms of oxidation of Ni_3S_2 to a nickel sulphide of lower nickel content,

$$Ni_3S_2 \longrightarrow Ni_{3-x}S_2 + xNi^{2+} + 2xe^- \qquad (1)$$

It can be seen from Fig. 4 that the anodic process initially follows a Tafel relationship with a slope similar to that for nickel electrodes and this suggests that Reaction 1 proceeds through a similar path to nickel dissolution.

The stable phases at ambient temperature in the nickel/sulphur system following heazlewoodite (Ni_3S_2) are godlevskite (Ni_7S_6) and millerite (NiS) [12, 13]. The standard potential calculated for Reaction 1, based on the thermodynamic data reported by Vaughan and Craig [14], is 0.18 V and 0.14 V above that of the Ni/Ni^{2+} couple when the $Ni_{3-x}S_2$ product is taken as Ni_7S_6 and NiS, respectively. Since the potential for NiS formation is lower than that for Ni_7S_6, the latter phase would be expected to be unstable. However, this conclusion is dependent on the reliability of the free energy values of the various sulphide species involved. Note that the standard potential for the Ni_3S_2/NiS couple is 0.17 V based on the data of Pankratz *et al.* [15].

It is possible that a metastable nickel sulphide phase is formed in Reaction 1, as occurs in the oxidation of chalcocite (Cu_2S) [16]. Such metastable phases could be related to the high temperature $Ni_{3\pm x}S_2$ and $Ni_{4\pm x}S_3$ phases in the nickel/sulphur system [12, 13]. The open-circuit potential of the Ni_3S_2 electrode, after holding the potential at 0.2 V for 1 min to form some oxidized nickel sulphide, was 0.09 V more positive than that of a nickel electrode in the same solution. This value is consistent with a metastable phase as oxidation product but does not rule out Ni_7S_6 or NiS due to the lack of precision of the potentials calculated from the reported free energy values. The current for the Ni_3S_2 electrode in Fig. 4 is not strongly inhibited by the initial nickel sulphide product, although a departure from Tafel behaviour becomes evident above ~0 V. However, the current peaks at ~0.2 V and then falls by more than an order of magnitude over the next 0.4 V. This behaviour can be explained by further oxidation of the nickel sulphide to deposit a passivating layer of another sulphide of lower nickel content or elemental sulphur on the electrode surface.

The current in Fig. 4 for the nickel sulphide electrode increases again at about 0.55 V. This probably arises from further oxidation of the product sulphur to sulphate,

$$S + 4H_2O \longrightarrow SO_4^{2-} + 8H^+ + 6e^- \qquad (2)$$

The current-potential curves from Fig. 1 for sintered anodes containing high and no added sulphur are included in Fig. 4. An exact comparison between the behaviour of the two systems is not possible; the data for the sulphide electrode must be obtained with a freshly abraded surface whereas those for sintered anodes covered with a sulphur layer requires some nickel to be dissolved in order to be fully activated through accumulation of sulphur at the surface. The latter treatment inevitably results in changes in surface roughness. However, it is clear from Fig. 4 that the current observed for the sintered anode containing sulphur is close to that for Ni_3S_2 in the low potential region. Inhibition due to further oxidation of the nickel sulphide product is not observed for the nickel electrode with added sulphur and this can be explained by Ni_3S_2 being continually regenerated by reaction with underlying elemental nickel,

$$Ni_{3-x}S_2 + xNi \longrightarrow Ni_3S_2 \qquad (3)$$

The results of these studies suggest that catalysis of anodic nickel dissolution by sulphur could arise via Reactions 1 and 3. Reaction 1 has a reversible potential 0.09 V more positive than that of nickel dissolution but this disadvantage would be nullified by less than a seven-fold increase in exchange current density, i_0, (Tafel slope = 110 mV). Extrapolation of the Tafel lines in Fig. 4 to the observed reversible potentials indicate that the i_0 for Ni_3S_2 is about three order of magnitude greater than that for the nickel electrode containing no added sulphur. Thus, a surface layer of Ni_3S_2 will significantly enhance nickel dissolution provided the layer is sufficiently thin to allow ready diffusion of nickel from the underlying metal.

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