JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 8–15

Activated basket anodes from nickel powder
Part II: Fabrication of anodes by a liquid phase sintering process

I. J. BEAR, R. C. FLANN, K. J. McDONALD, L. J. ROGERS, R. WOODS
CSIRO Division of Mineral Products, P.O. Box 124, Port Melbourne, Victoria 3207, Australia

Received 15 March 1991

A process has been developed for the fabrication of sulphur activated basket anodes from nickel powder for use in the electroplating industry. These anodes have satisfactorily high anode current efficiency, lead to high cathode current efficiency, give good quality electroplate and yield anode residues of 0.5% or less.

1. Introduction

Basket anodes are commonly employed in modern nickel electroplating practice. Preferably, such anodes should be of suitable size and shape to be accommodated in standard titanium mesh anode baskets, should not have sharp edges or protrusions that may damage the anode bags, and they should dissolve in the electrolyte at high anode current efficiency with the generation of very little anode residue. In addition, they should give rise to high cathode current efficiency and good quality electroplate. Electroformed, sulphur depolarised anodes of various shapes meet these criteria and are used extensively in commercial electroplating operations.

During earlier work in these laboratories, a method [1] was developed for producing basket anodes from precipitated nickel powder. The powder was high purity nickel (99.8%) produced by the Sherritt Gordon Process at the Western Mining Corporation Limited (WMC) Refinery at Kwinana in Western Australia. The process involved heating the powder prior to compaction at a temperature in the range 550–960° C in an inert or reducing atmosphere [2]. This treatment eliminated gas-generating impurities (Table 1) that caused disruption of particles and particle–particle bonds during subsequent sintering of the compacts [3]. The preheated powders were compacted, either cold or hot, at 463 MPa and sintered at 960° C in a hydrogen atmosphere.

Anodes produced by this sintered nickel powder (SNP) process gave excellent cathode plate and met all but one of the specified criteria. The criterion they did not meet was the amount of anode residue they generated, which was large (1–5%) compared with that from commercial, sulphur depolarised anodes (less than 0.5%). The residue, unlike the fine black sludge produced by sulphur depolarised anodes, was clean and consisted essentially of metallic nickel. But, as nickel is a high-value metal, these anodes would be unlikely to succeed in the market place.

Part I of this series of papers [4] describes the methods developed for assessing anode performance in the laboratory. The present paper describes the laboratory-scale development of a liquid phase sintering process (LPS process) designed to overcome the residue problem; Part III presents a study on the electrochemical behaviour of these anodes, while Part IV concerns the scaling-up of the LPS process and discusses the performance of the anodes in an industrial electroplating circuit.

2. Background to the process

In the SNP process, the preheat-treatment of the powder causes cracking of the powder particles, as can be seen from the scanning electron microscope (SEM) photomicrographs in Fig. 1. The micrograph in Fig. 1a is of whole powder particles, whereas that in Fig. 1b is of a sectioned, preheated particle and reveals its cracked and fragmented nature [3, 5]. These cracks and fragments are welded together again during the sintering of the preheated-powder compact (Fig. 1c).

Microscopic examination of the residue generated by anodes produced by the SNP process has shown that it is composed largely of hollow shells of particles (Fig. 2a) small remnants (Fig. 2b and 2c) as well as pieces of surface "skin" from the compact (Fig. 2d). As the residue contains relatively few whole powder particles, it is not generated by the preferential electrolytic corrosion of the junctions, or "necks", between particles in the sintered compact. It seems, rather, that the outer surfaces of the particles and the neck regions become passivated, so that the anode does not dissolve uniformly.

It is well established that the presence of sulphur in nickel anodes can improve their performance by preventing the formation of passive surface films during their electrolytic dissolution [6, 7]. As will be discussed more fully in Part III of this series, sulphur enhanced corrosion of nickel has been shown to result from the

0021-891X/92 $03.00 + .12

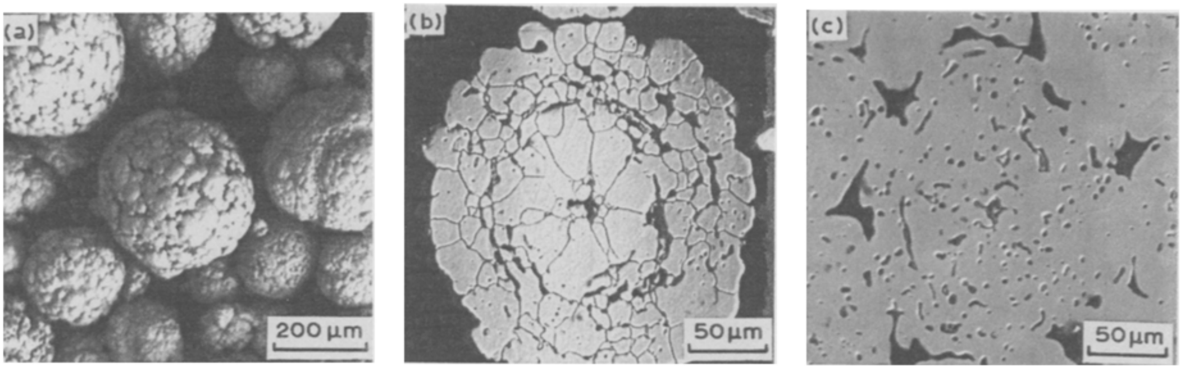

Fig. 1. SEM photomicrographs of: (a) whole nickel powder particles (b) sections through particles after they have been heat-treated in an atmosphere of nitrogen at 960° C, (c) section of a sintered compact of preheated powder.

formation and retention, during dissolution, of a nickel sulphide on the surface of the anode [8, 9].

The as-received nickel powder used in the present work contains 170–240 p.p.m. sulphur (Table 1). Although little of this sulphur is lost during preheat-treatment of the powder in nitrogen [5], most of it is removed as hydrogen sulphide during sintering of the powder compacts in a hydrogen or syngas (3 parts by volume hydrogen and 1 part nitrogen) atmosphere, residual sulphur being as low as 10 p.p.m. Further, this residual sulphur may not be uniformly distributed throughout the sintered compact, because, during sintering, sulphur will be removed first from those regions most accessible to the sintering atmosphere, i.e. from the surface layers of the compact and from the surfaces of individual particles where the gases can diffuse readily along grain boundaries and through open pores in the compact. If sulphur is lost from these regions more rapidly than it can be replaced by solid state diffusion of sulphur from the interior of the metal, the surface of the particles will be left deficient in sulphur.

Consequently, during electrodissolution of the sintered compact, the sulphur deficient regions can become passivated so that the compact does not dissolve uniformly. Such an occurrence could account for the nature of remnants found in the residues of anodes produced by the SNP process (Fig. 2).

It seemed, therefore, that if the anode residue were to be decreased, it would be necessary to design a sintering process that would ensure that there was an adequate supply of sulphur in the form of nickel sulphide on all internal and external surfaces of the nickel particles in the sintered compacts. Various methods for incorporating sulphur in the compacts were, therefore, evaluated.

It became evident that the best and possibly the most economical means of achieving the desired result was to heat the powder at an elevated temperature in an atmosphere of syngas containing a low partial pressure of hydrogen sulphide. The hydrogen sulphide reacts with the nickel forming a layer of Ni_3S_2 on the surfaces of the powder particles.

The presence of nickel sulphide at the interfaces

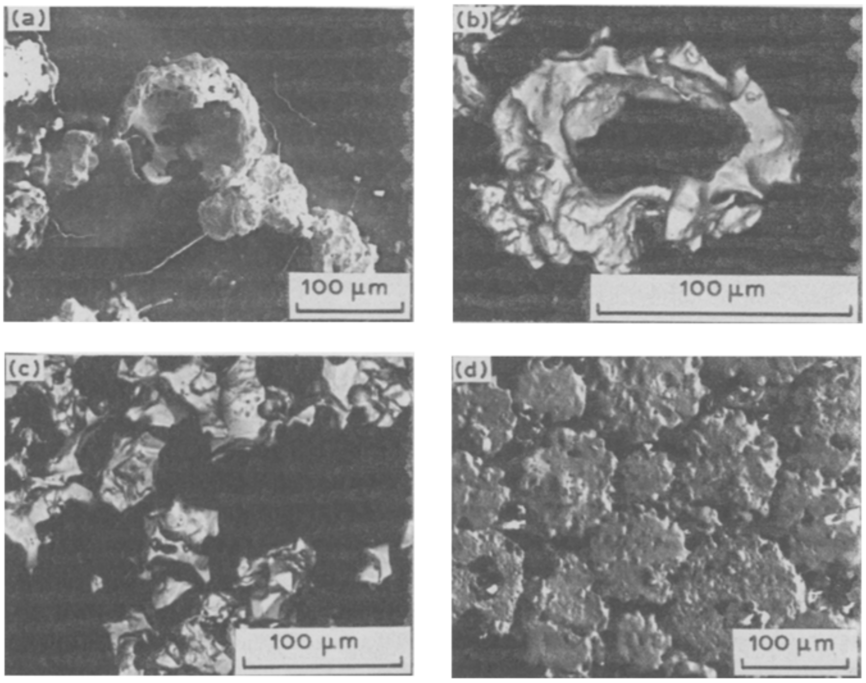

Fig. 2. SEM photomicrographs of anode residue from an anode produced by the SNP process: (a) hollow shell of a particle; (b and c) particle remnants; (d) piece of surface "skin" from the anode.

Table 1. Impurity content of precipitated nickel powder, 99.8% nominal purity

Metal	*Concentration (p.p.m)*	*Non-metal*	*Concentration (p.p.m)*
Copper	3–5	Sulphur	170–240
Cobalt	50–70	Carbon	40–110
Iron	4–6	Oxygen	400–700
		Hydrogen	~5
		Nitrogen	~50

between particles in the compact has the added advantage that sintering can proceed via a liquid phase [10, 11]. This is because there is an eutectic point in the nickel-sulphur system [12, 13] at 637° C, well below the sintering temperature for the compacts of 960° C. A film of liquid that wets the particles can facilitate the sintering process by enhancing the rate of interdiffusion of nickel.

Other approaches investigated for incorporating sulphur included: mixing the nickel powder with elemental sulphur, coating the particles with nickel sulphate by placing them in an aqueous solution of the compound and evaporating the water (the sulphate reduces to sulphide well below the sintering temperature) and mixing powdered Ni_3S_2 with the nickel powder prior to compaction of the mixture. Another approach was to sulphidise the powder after compaction. In each case, the sulphur was not as uniformly distributed as when the nickel powder was sulphidised with hydrogen sulphide.

3. The LPS process

3.1. *Process outline*

The LPS process developed for producing "sulphur depolarised" basket anodes from nickel powder incorporates the following steps:

1. Heat-treatment of the as-received precipitated nickel powder in a nitrogen atmosphere at approximately 750° C for 30 min to remove gas-generating trace impurities.
2. Sulphidisation of the surface of the preheat-treated powder particles at 380° C in a mixed nitrogen-hydrogen (50 : 50, v/v) atmosphere containing hydrogen sulphide in the volume ratio of one part to one hundred parts hydrogen. The preferred extent of sulphidisation is 1500–2000 p.p.m. S.
3. Mixing of the sulphidised powder with a lubricant (0.25% nickel stearate) and compaction of the mixture into any desired shape to produce compacts with a green density of approximately 86% that of solid nickel. Typically, 15 g samples of the mixture were pressed at 616 MPa into discs 25 mm in diameter and approximately 4 mm thick.
4. Sintering of the compacts in a syngas atmosphere at (960 ± 5)° C, with the concomitant removal of sulphur as hydrogen sulphide to give a residual sulphur content in the sintered compacts in the range 200–400 p.p.m. S. A sintering period of one hour is generally adequate for this purpose.

3.2. *Materials and procedure*

The several batches of nickel powder used in developing the process were donated by WMC and had similar properties to those of powder used in earlier studies [1–5]. Briefly, the powder was high purity (99.8%) commercially precipitated nickel powder with impurity concentrations within the ranges indicated in Table 1 and with 88% of the essentially spherical particles falling within the size-range 43–147 μm. Nickel stearate lubricant was prepared and donated by Fletcher Chemical Company Ltd of Melbourne, Australia. High purity nitrogen, hydrogen and hydrogen sulphide cylinder gases were from The Commonwealth Industrial Gases Limited.

In Step 1 200 g batches of the nickel powder were heated in a silica boat in a horizontal, electrically heated, silica tube furnace (silica reactor, 43 mm in diameter). The nitrogen flow rate was 550 cm^3 min^{-1}.

Sulphidisation of the 200 g batches of preheated powder (Step 2) was done in a vibrated silica tube reactor, mounted vertically in an electrically heated furnace, with the sulphidising atmosphere entering through a lance to the base of the moving bed of powder (Fig. 3). Atmosphere sparging rate was approximately 600 cm^3 min^{-1}. The extent of sulphidisation was monitored semi-quantitatively by comparing the intensity of the (012) X-ray peak for Ni_3S_2 in the diffractogram of the sulphidised powder with the intensity of the same peak in the diffractogram of a reference sample of powder containing a known quantity of sulphide sulphur. A Leco Model CS244 carbon/sulphur analyser was used for the quantitative determination of sulphur in the final product.

Details of the die and press used for compaction of the powders have been given previously [1], while sintering of the compacts, generally in groups of three, was achieved in the same furnace as used for the preheat-treatment of the powders. Syngas flow rate was 550 cm^3 min^{-1}.

Sintering procedure was to: place the compacts flat on a strip of inconel mesh belt or on a silica boat (so gases could pass over and under the compacts) in the cold furnace; flush the sample chamber with nitrogen for 10 min before introducing hydrogen to the atmosphere; switch on the power and bring the compacts to the sintering temperature in approximately 45 min; hold the compacts at this temperature for the desired period. It is important to the subsequent discussion to note that, at the end of the sintering period, the power to the furnace was switched off and the compacts allowed to cool to less than 60° C in the sintering atmosphere. The temperature of the furnace dropped to 600° C (i.e. below the eutectic temperature of the Ni–S system) in approximately 25 min.

Individual sintered compacts were tested as basket anodes in the small laboratory electroplating facility,

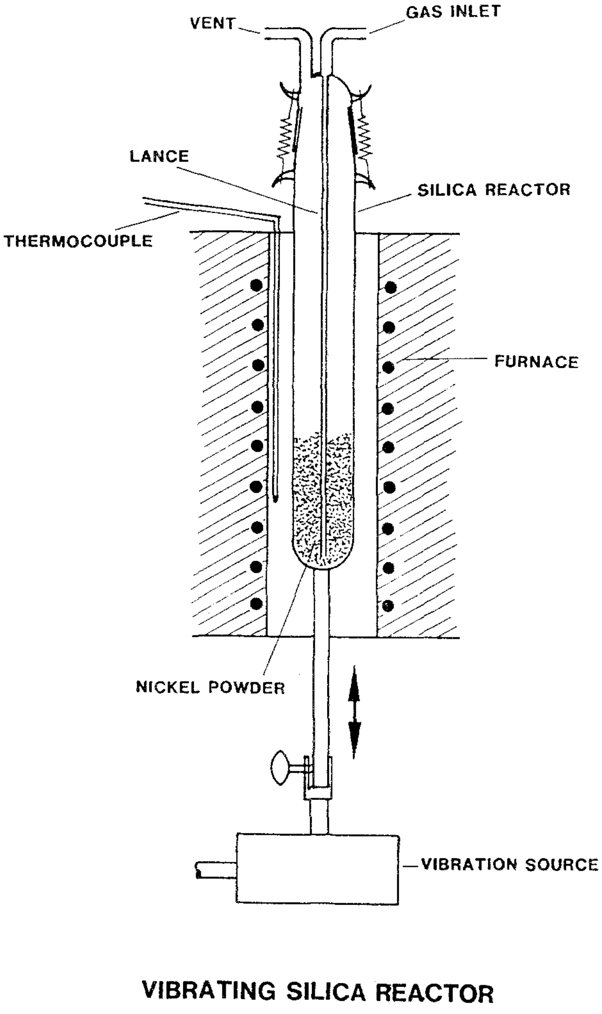

Fig. 3. Apparatus used for the laboratory scale sulphidisation of nickel powder.

described in Part I of this series [4]. Commercial electrolytes and additives from Oxy Metal Industries (Australia) Pty Ltd were used – either a Bright Watts type bath (Nickel 66) for the electrodeposition of nickel only, or a Niron bath (Niron H) for the electrodeposition of a nickel-iron alloy.

Anodes gave comparable performance in both kinds of bath. The current density based on cathode area was 300 A m^{-2}, which is the average commercial value. In the analysis of anode materials and cathode plate, metal values were determined by atomic absorption spectrometry.

4. Anode performance and discussion

In developing the LPS process, confirmation was sought that a liquid phase does form during the sintering stage of the process. Consequently, a compact containing approximately 3000 p.p.m. sulphur was sintered in a nitrogen atmosphere at 960° C for 1 h. As the nitrogen atmosphere does not remove sulphur from the compact, any liquid phase formed should remain and solidify in the interstices between the particles. Figure 4a, which is a SEM photomicrograph of a small area of a section through the sintered compact, provides clear evidence that a liquid phase did form, although at the sulphur concentration employed most large voids were not filled with liquid. Figure 4b is a photomicrograph of a similarly prepared compact except in this case the sintering atmosphere was syngas. The latter atmosphere ensures more rapid interdiffusion of nickel and also removes a substantial proportion of the sulphur. If the sulphur is reduced to the preferred level, nickel sulphide can rarely be identified when examining the sintered compact in the SEM or by X-ray diffraction.

Sulphidised nickel powder containing a higher than desired level of sulphur can be blended with preheated powder that has not been sulphidised without detrimentally affecting the performance of the anodes. For instance, powder containing 3000 p.p.m. sulphur was blended with an equal weight of non-sulphidised powder to yield a mixture containing 1500 p.p.m. sulphur. Further, the diluent powder need not necessarily be of the same particle size as is the sulphidised powder. Nickel powder that had been reduced in particle size by grinding [14] so that 90% passed 44 μm was successfully blended with sulphidised powders.

When nickel compacts prepared by the LPS process were tested individually as anodes, they gave satisfactory anode and cathode current efficiencies and good quality cathode-plate. Anode residues were generally 0.5% or less. A typical set of results for anodes prepared by the LPS and SNP processes and commercial electroformed Inco "S" nickel rounds is given in Table 2.

Anode potentials (against a standard calomel electrode, SCE) were measured during the electroplating trials. The commercial 'S' Ni and the LPS (1) anodes listed in Table 2 both dissolved at approximately

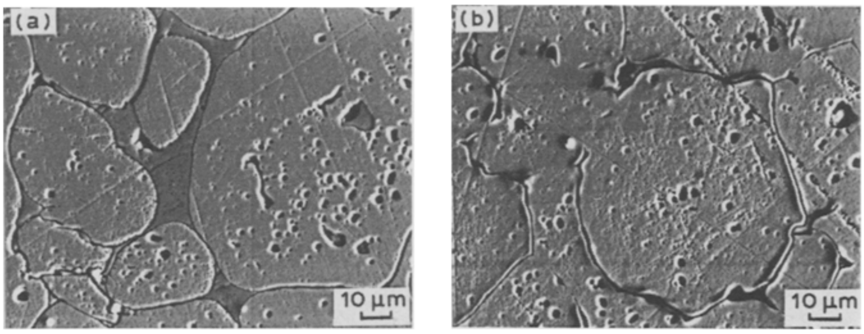

Fig. 4. SEM photomicrograph of: (a) section through a compact of preheated, sulphidised nickel powder after sintering in nitrogen at 960° C; (b) as for micrograph (a) but sintered in syngas.

Table 2. Data from electroplating tests on basket anodes*

Anode type	*Composition*	*Sulphur in anode (p.p.m.)*	*Current efficiency (%)*		*Anode residue (%)*
			Anode	*Cathode*	
SNP	preheated powder	~6	101.4	92.3	4.0
LPS (1)	sulphidised powder (2069 p.p.m. S)	610	101.3	93.1	0.35
LPS (2)	70% sulphidised powder plus 30% ground powder	280	100.8	94.5	0.42
'S' Ni	commercial electroformed	340	101.5	87.7	0.12

* Niron electrolyte

−0.2 V. On the other hand, the potential of the SNP anode remained near zero for the first 3 h, rose steeply over the following 3 h to approximately +0.3 V, then continued to increase slowly throughout the test. The anode, LPS (2), exhibited a dissolution potential intermediate to those noted above; it was zero at the beginning of the experiment, but dropped over the first 5 h to settle near −0.1 V.

These results confirm that the LPS process produces a basket anode that is more electrolytically active and yields a considerably lower anode residue than one produced by the SNP process. They also show that properties of LPS anodes are similar to those of commercial 'S' rounds (see also Part III of this paper).

An activated sintering process for producing nickel anodes has been described in a Japanese patent [15]. The CSIRO LPS process differs from the Japanese process in two main respects. One is the preferred sintering temperature: CSIRO, (960 ± 5)° C; Japanese, in the range 1050–1400° C, with examples quoted at 1200° C. The other is that the CSIRO compacts are cooled relatively slowly from the sintering temperature, whereas the Japanese compacts are quenched in a liquid (e.g. water or oil).

Although an extensive examination of the relative merits of the two processes has not been undertaken, a few comparative tests have been made. For example, four sets of three green compacts were prepared as for the LPS process from the same stock of sulphidised nickel powder containing approximately 2300 p.p.m. sulphur. Two were sintered in syngas at 1100° C (within the Japanese specification) and two at 960° C (CSIRO specification). One set from each pair was quenched from the sintering temperature in water, the other cooled slowly in the sintering atmosphere.

In the quenching experiments, after the compacts had been sintered in syngas for 1 h at the specified sintering temperature, the reactor was flushed with nitrogen for 10 min before the compacts were plunged through a nitrogen atmosphere into water. One sintered compact from each set was tested as an anode. The anode residues and other relevant data obtained in these tests are given in Table 3. The residues noted in Table 3 make it abundantly clear why the specifications for the two processes differ. The compact quenched from 1100° C gave a much lower anode residue than the compact that was cooled slowly. Conversely, the compact quenched from 960° C gave a higher anode residue than the one that was cooled slowly.

The reason for the difference in behaviour is not yet understood, but from examination of anode remnant lumps from electro-dissolution of the compacts it appears to be related to the mode of electrolytic dissolution of the anodes (Fig. 5). It is apparent that in the anodes generating the higher residues (Fig. 5a and d) selective dissolution occurred along grain boundaries around particles, whereas in the lower residue anodes

Table 3. Properties of compacts cooled slowly or quenched from sintering temperatures of 960° C and 1100° C

Property	*960° C*		*1100° C*	
	Cooled slowly	*Quenched*	*Cooled slowly*	*Quenched*
Density (% of solid)	81.7	81.8	82.2	82.1
Volume expansion on sintering (%)	4.9	4.8	4.0	4.7
Total sulphur (p.p.m.)	368.0	463.0	515.0	697.0
Estimated sulphur evolved during cooling (p.p.m.)	95.0		182.0	
Anode residue (%)	0.5	1.1	4.9	0.4
Anode current efficiency (%)	101.3	101.1	101.8	101.0
Cathode current efficiency (%)	93.1	91.1	92.3	92.3

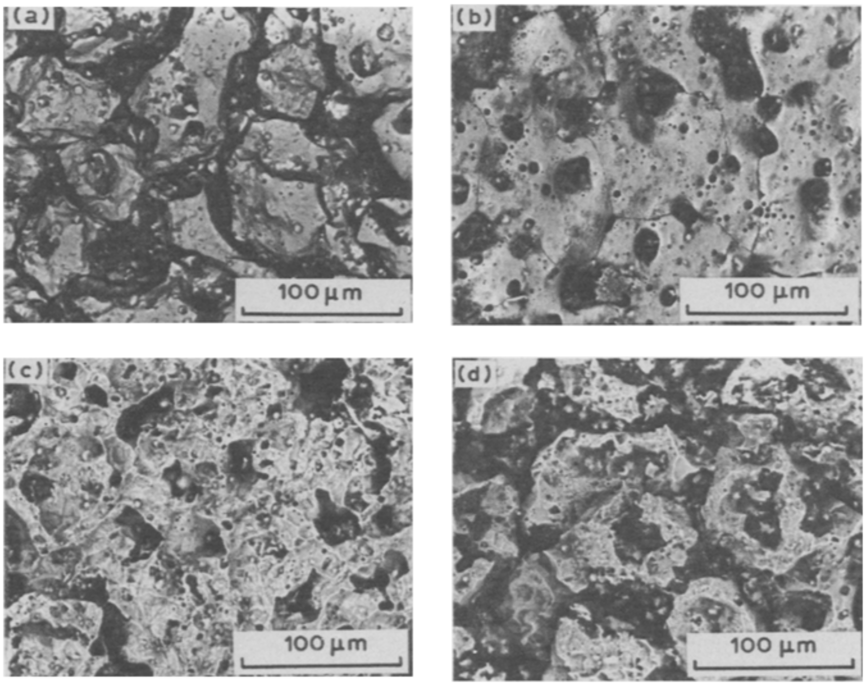

Fig. 5. SEM photomicrographs of anode residue lumps from compacts sintered at: (a) 1100° C, cooled slowly; (b) 1100° C, quenched; (c) 960° C, cooled slowly; (d) 960° C, quenched.

(Fig. 5b and c) dissolution occurred more uniformly with random distribution of pits.

There is no obvious correlation between the amount of anode residue and other information given in Table 3. All compacts gave high anode and cathode current efficiencies. As might be expected, the compacts sintered at 1100° C are slightly denser than those sintered at 960° C and, in keeping with the density values, the overall volume expansion during sintering is slightly less at 1100° C than at 960° C. Further, there is no obvious correlation between the level of anode residue and the residual sulphur in the compacts. The amount of residual sulphur in the compacts sintered at 1100° C is higher than that in the compacts sintered at 960° C. This probably results from a combination of causes — interdiffusion of nickel will be more rapid at the higher temperature, resulting in more rapid pore closure (as indicated by the slightly higher densities of the compacts sintered at 1100° C) and the solid solubility of sulphur in nickel is greater at the higher temperature [16]. Both these effects are likely to impede the removal of sulphur from the compacts by the sintering atmosphere. It is also noticeable that the slowly cooled compacts contain less sulphur than their quenched counterparts, which indicates that sulphur continues to be removed by the sintering atmosphere during the slow cooling process; the amounts eliminated, estimated in each case from the difference between the residual sulphur value for the quenched and slow-cooled compact, are noted in Table 3.

In seeking an answer to the observed differences in anode behaviour it is interesting to consider the location and movement of sulphur and the precipitation/dissolution of nickel in the grain boundaries during the heating and cooling cycle of the sintering process. The added sulphur is present in the green compact as Ni_3S_2(73.3% Ni, 26.7% S) and is located at inter-particle boundaries, in open pores of the powder particles and on the surfaces of cavities in the compact.

When the temperature of the compact reaches the eutectic temperature (ET) in the nickel-sulphur system (637° C; composition 78.5% Ni, 21.5% S [12, 13]) liquid will form and additional nickel will be brought into the sulphide solution. Above the eutectic temperature several reactions take place concomitantly:

(i) Inter-atomic diffusion becomes relatively rapid [17] with sulphur diffusing into the nickel particles to the limit of its solid solubility in nickel (in weight, approximately 30 p.p.m. at ET, 200 p.p.m. at 960° C and 350 p.p.m. at 1100° C [16]). The movement of sulphur away from the grain boundaries and interstices causes nickel to precipitate from the melt in order to maintain the liquidus composition.

(ii) Sulphur will be removed from the liquid as hydrogen sulphide by the sintering atmosphere. Again, nickel will be precipitated from the melt to compensate for the loss of sulphur.

(iii) The composition of the melt will change as the temperature increases and the composition at the liquidus changes (approximately, 81.8% Ni, 18.2% S at 960° C and 84.4% Ni, 15.6% S at 1000° C [12, 13]). Thus, the amount of nickel brought into solution will increase with increase in the sintering temperature.

If equilibrium of sulphur solubility in nickel were achieved during sintering (and equilibrium will be approached more readily at 1100° C than at 960° C) compacts cooled by quenching should exhibit the sulphur and nickel distribution pertaining to conditions existing at the end of the sinter period. In the case of the slowly cooled compacts on the other hand, reaction (ii) above will continue during cooling, reactions (i) and (iii) will be reversed and further

Table 4. Sulphur and nickel distribution in compacts quenched and slow cooled from 960° C and 1100° C

Property	*Concentration* (*weight p.p.m.*)	
Sintering temperature	960° C	1100° C
(*a*) *Quenched* (*equilibrium values*)		
Total sulphur	463	697
Sulphur in solid solution	200	350
Sulphur in grain boundaries as Ni_xS*	263	347
Nickel in grain boundaries as Ni_xS	1183	1879
Total Ni_xS	1446	2226
(*b*) *Slow cooled* (*equilibrium values*)		
Total sulphur	368	515
Sulphur in solid solution	30	30
Sulphur in grain boundaries as Ni_3S_2	338	485
Nickel in grain boundaries as Ni_3S_2	928	1333
Total Ni_3S_2	1266	1818
Nickel precipitated in grain boundaries below ET	306	438

* From phase diagram [12, 13] Ni_xS is approximately $Ni_{1.99}S$ at the eutectic point (ET), $Ni_{2.45}S$ at 960° C and $Ni_{2.95}S$ at 1100° C.

ex-solution of nickel will occur in the grain boundaries when the compact cools through the ET. It should be noted that the high temperature $Ni_{3\pm x}S_2$ phase is non-quenchable [12] so that the final grain boundary product should be a mixture of Ni_3S_2 and Ni.

On the basis of the above reactions and assumptions, the distribution of nickel and sulphur in the sintered compacts can be estimated; the details are given in Table 4. In both compacts cooled by quenching the sulphur in the grain boundaries is combined in a nickel sulphide phase of composition specific to the sintering temperature, i.e., approximately $Ni_{2.95}S$ at 1100° C and $Ni_{2.45}S$ at 960° C.

Considering the quenched compacts, it is evident from the data in Table 4 that not only is there more sulphur present in the compact quenched from 1100° C than there is in that quenched from 960° C, but also it is more uniformly distributed between the bulk of the metal and the grain boundaries. Further, the concentration of sulphur in the liquid phase at 1100° C is significantly less than it is in the liquid phase at 960° C. Overall, in weight p.p.m., there is in excess of 50% more liquid phase component in the 1100° C quenched compact than there is in the 960° C quenched compact, so the sulphur is likely to be distributed more extensively throughout the grain boundaries and interstices of the former compact than it is in the latter. This more even and extensive distribution of sulphur may account for the more uniform electrolytic dissolution of the 1100° C quenched compact compared with that of the 960° C quenched compact.

However, the above observations only apply to quenched compacts where substantial equilibrium is likely to have been achieved before quenching. Those features in quenched compacts that are favourable for the production of low residue anodes may not be favourable for that purpose in the case of slowly cooled compacts where non-equilibrium conditions prevail. It is known that non-equilibrium segregation of sulphur to the grain boundaries in nickel can produce striation and faceting of the boundaries [18] embrittlement of the metal [17] and intergranular corrosion [19].

In the present case, as the compact cools and the solid solubility limit of sulphur in nickel decreases, much of the sulphur in solution is likely to precipitate *in situ*. Nevertheless, during the cooling process there will be continual material transport of sulphur to, and vapour transport of sulphur away from, the grain boundaries; these movements of sulphur will be accompanied by the dissolution and precipitation, respectively, of nickel. The perturbations at the grain boundaries in the compact sintered at 1100° C, which contains the larger amount of sulphur, are likely to be much more severe than they are in the compact sintered at 960° C. Apart from the movement of sulphur, it is estimated that more than twice as much nickel would be dissolved and more than twice as much nickel precipitated during the cooling of the compact sintered at 1100° C than would occur during the cooling of the compact sintered at 960° C. Thus, preferential grain boundary corrosion is more likely to occur in the former case than in the latter. Clearly, further work is required to substantiate these possibilities.

Although a detailed investigation of the performance and production costs of the products from the CSIRO and Japanese processes would be necessary to fully evaluate their relative market potential, the lower energy consumption of the CSIRO process should give it an advantage commercially.

Acknowledgements

The authors thank Western Mining Corporation Limited for some financial support for the project and for donation of the nickel powder; they are indebted to Fletcher Chemical Co., Ltd for the special production and donation of nickel stearate, and to Mr J. Kleine, then of Parker Chemicals Ltd, for advice on the electroplating tests and the supply of commercial electrolytes and additives. They acknowledge contributions to the project by colleagues in the analytical, SEM sample preparation and photographic services sections of the Division.

References

[1] I. J. Bear and R. C. Flann, Proc. The Aus I.M.M. Conference, Western Australia, August (1979) 89.
[2] I. J. Bear and R. C. A. Flann, Australian Patent No. 527632 (1979).
[3] I. J. Bear, R. C. Flann and L. J. Rogers, *Powder Metallurgy* No. 2 (1980) 71.
[4] I. J. Bear and R. C. Flann, *J. Appl. Electrochem.*, 961.
[5] I. J. Bear and R. C. Flann, Proc. P/M-82 in Europe Intern. Powder Metall. Conference, Florence, June (1982) 289; *Fachberichte für Metallbearbeitung* **60** No. 11–12 (1983) 494.
[6] C. M. Whittington, *Metals Australasia* September (1979) 26; October (1979) 21.
[7] R. Parkinson, *Electroplating and Metal Finishing* February (1974) 9.

[8] P. Marcus, J. Oudar and I. Olefjord, *Mater. Sci. Eng.* **42** (1980) 191.
[9] D. R. Baer and M. J. Danielson, *J. Vac. Sci. Technol.* **A5** (1987) 1147.
[10] R. M. German, 'Liquid Phase Sintering' (Plenum Press, New York, 1985).
[11] W. A. Kaysser and P. Petrow, *Powder Metallurgy* **28** No. 3 (1985) 145.
[12] G. Kullerud and R. A. Yund, *J. Petrology* **3** Part 1 (1962) 126.
[13] R. C. Sharma and Y. A. Chang, *Met. Trans.* **11B** (1980) 139.
[14] I. J. Bear, R. C. A. Flann and R. Bartholomeusz, *Powder Metall. Inter.* **14** No. 4 (1982) 207.
[15] T. Nobunari, M. Hideaki, Y. Masaki and O. Toshihiko, Japanese Patent 78-3904 (1978).
[16] R. J. Brigham, H. Neumayer and J. S. Kirklady, *Can. Met. Quarterly* **9** (1970) 525.
[17] R. A. Mulford, *Met. Trans.* **14A** (1983) 865.
[18] C. Loier and J. Y. Boos, *Met. Trans.* **12A** (1981) 129.
[19] H. Chaung, J. B. Lumsden and R. W. Staehle, *Met. Trans.* **10A** (1979) 1853.