Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 123 (2003) 253–260
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

The preparation of highly porous structures from filamentary nickel powders

A.Y. Zaitsev [a,*], D.S. Wilkinson [a], G.C. Weatherly [a,†], T.F. Stephenson [b]

[a] *McMaster University, 1280 Main Street West, Hamilton, Ont., Canada L8S 4L7*
[b] *INCO Technical Services, 2060 Flavelle Boulevard, Mississauga, Ont., Canada L5K 1Z9*

Received 10 March 2003; accepted 30 March 2003

Abstract

Porous nickel structures are in high demand for battery, catalyst and filter materials applications. Traditionally such structures are made by sintering fine filamentary nickel powders. However, the strength of such structures is rather low, when compared, for example, with Ni foams of similar density. In this research we have applied colloidal processing techniques to improve the powder particle distribution and, hence the strength of the final sintered structure. By dispersing Ni powder in water prior to introducing a binder, better separation of particles and break-up of conglomerates is achieved. The addition of dispersants further improves the particle distribution. The new method also enhances control of the slurry viscosity and the green density of the nickel porous body. The structure of battery plaque prepared according to the new technique is therefore more uniform than the structure of the conventional plaque. Moreover, the tensile strength of a plaque prepared by the new method is increased by 50–70%.

Keywords: Porous nickel; Sintering; Batteries; Positive electrode

1. Introduction

Nickel powders having a highly irregular filamentary shape can be fabricated and sintered to produce highly porous structures, which are in high demand for battery, catalyst and filter materials applications. In addition to high porosity these materials offer excellent corrosion resistance and good electrical conductivity. One of the most important requirements for these types of structures is the combination of high strength while maintaining a level of high porosity, especially for the case of rechargeable batteries. The charge-carrying capacity of batteries is strongly dependent on the amount of active mass impregnated in the porous plaque while battery lifetime is sensitive to the strength of the porous structure. This must be sufficient to withstand repeated swelling and shrinking during battery charging and recharging cycles without failure [1].

The traditional approach to the manufacture of such structures is by sintering of fine filamentary nickel powders. The dominant technology in commercial production involves a highly automated and economical slurry coating process onto a perforated substrate. Though detailed information on the technical aspects of this process is limited due its proprietary nature, it is known that electrode plaque production process based on the use of the Inco Type 255 filamentary nickel powder involves several main steps [2]:

- preparation of a slurry by mixing the nickel powder in an aqueous cellulose solution,
- coating of a perforated metal substrate (typically made of nickel-coated steel) with the slurry using a vertical tape casting process (twin doctor blades are used to control the coating thickness),
- drying the slurry in an oven at temperatures below 100 °C, and
- sintering in a reducing atmosphere at a temperature of about 1000 °C.

An example of the sintered nickel plaque produced by such a process is given in Fig. 1. The plaque was produced by a commercial vendor and is thought to be typical of those employed in industrial practice. A very similar microstructure is observed in plaques produced in our laboratory by the process just described.

The structure of this plaque includes large voids (up to about 100 μm in diameter). There are several disadvantages in producing such a non-uniform structure, including:

* Corresponding author.
† Deceased.
E-mail address: azaitsev@inco.com (A.Y. Zaitsev).

0378-7753/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0378-7753(03)00534-2

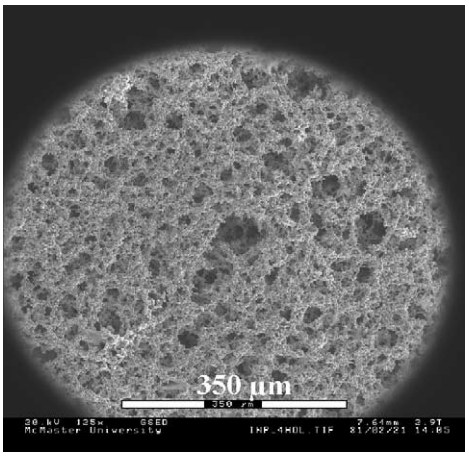


Fig. 1. Microstructure of a sintered industrial plaque (×125).

- decreased battery efficiency due to difficulty in discharging and recharging the active mass far from the conducting phase, and
- decreased strength due to uneven stress concentrations.

Hence, the performance of a battery (or filter) prepared using this procedure may be significantly degraded compared to its full potential.

2. Improving plaque microstructure

An answer to the problem indicated above is proposed in this paper. The solution involves improvements in particle distribution that provide a more even and hence, stronger structure, without sacrificing the desired overall porosity of about 80%. Altering the details of the sintering process (e.g. temperature, duration, sintering atmosphere) was found to have insignificant impact on the homogeneity of the final microstructure. We have therefore, focused on developing a new approach to slurry preparation using an adaptation of colloidal processing techniques to promote a uniform, dispersed powder distribution. In colloidal processing one uses surface-active chemicals as dispersant agents in an appropriate solvent (in this case all processing was aqueous-based) along with efficient mixing. Dispersants become attached to the surface of the particles leading to the emergence of repulsive forces between them. A suggested approach to processing is often used in ceramics for which the average particle size is about a micron or less [3]. It was not clear how well such an approach might work for filamentary nickel powders for which the dispersant must overcome the higher material density, large particle size (typical particle length is about 30 μm), and irregular shape. Despite these misgivings it was felt that this approach offered the potential of significant improvement in strength and homogeneity of sintered nickel electrodes.

A flow chart for the initial stages of the conventional electrode plaque preparation process is given in Fig. 2.

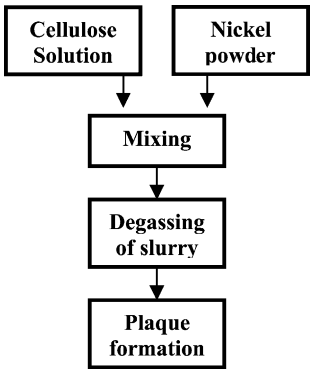


Fig. 2. Conventional method of plaque preparation.

In the first step nickel powder is mixed directly with the cellulose–water solution. Cellulose in this application plays the role of a binder between particles. The addition of cellulose is necessary in order to produce slurry of sufficient viscosity to enable the vertical tape casting process to proceed. Due to the filamentary structure of these nickel powders and relatively high viscosity of the cellulose solution the particles may be never well dispersed. Moreover, while intensive mixing can help disperse particles reasonably well, high shear stress may cause a filament breakage. The breakage of the filaments leads to the reduction of the sintered material porosity. In the process of the study it was found that the simple addition of dispersant agents into the solution during mixing does not lead to improvements in the structure, probably due to the competitive absorption of the cellulose contained in the starting solution. Thus, the dispersant is unable to become attached to the surface and develop repulsive forces between particles. Such phenomenon is a well known in the ceramic processing [4].

We have therefore developed a new processing sequence (Fig. 3) ensuring that the powder is well dispersed and the dispersant is attached to the particle surface before the binder phase is added. Moreover, in the new process, the initial mixing operation can be performed using high-speed stirring without filaments breakage due to the large excess of water present.

The proposed method of slurry preparation should not only allow good contact between dispersant and powder but also should enable control of the slurry rheological properties over a wide range of densities by adjusting both the concentration of cellulose in the solution as well as the amount of water used.

3. Experimental

A wide range of chemicals exists that might be suitable for use as dispersing agents to improve nickel powder dispersion. The efficiency of some of these was determined by measuring the Z-potential of Inco Type 255 nickel powder in aqueous media. The concentrations of dispersants were

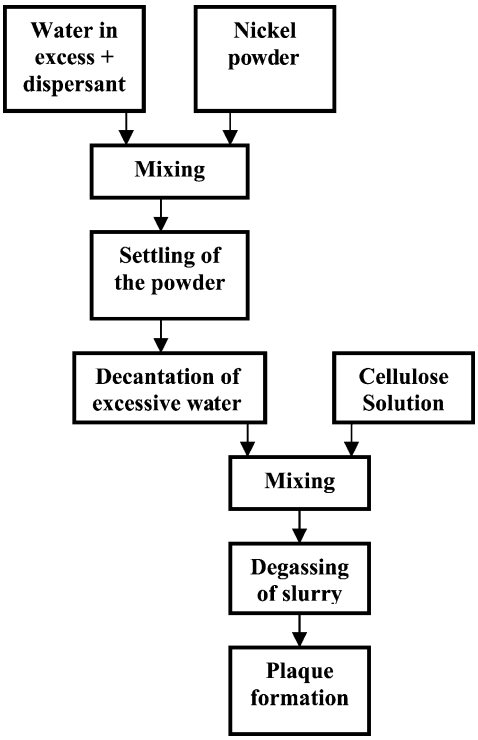


Fig. 3. Improved method of plaque preparation.

varied from 0 to 1% (by weight) based on the amount of nickel.

Dispersants used in this study were chosen from those commonly used in the ceramics and paint industry. These included several from the Darvan series (Darvan C, Darvan 821A, Darvan 811, provided by R.T. Vanderbitt Company) and the Polacryl series (A40-43N, A70-40N and B55-50 N, provided by Polacryl company). All of these are water-based and contain different forms of polyacrylate ammonium salts.

Nickel plaques were prepared according to the flow charts illustrated in Figs. 2 and 3. In the latter case, dispersant concentrations selected on the basis of the Z-potential measurements were used. Nickel powder was gradually mixed with water containing a known concentration of dispersant, in order to obtain good contact between the molecules of dispersant and nickel particles. The quantity of water was two to three times that which was necessary to produce final slurry of the required viscosity. After stirring, the powder was allowed to settle and the excess water was decanted to achieve the desired slurry composition, to which the cellulose solution was added. Table 1 shows the compositions of slurries used in these experiments (dispersant not included).

While commercial battery plaques always contain a metal substrate, we wished to manufacture plaques without substrates so that the strength of the sintered nickel bodies could be measured directly. Therefore, the slurry was cast into a green tape without a substrate using horizontal tape casting machine. After tape casting samples were dried at room temperature and sintered between 750 and 1050 °C for 10 min in a reducing atmosphere of 15% H_2 and 85% N_2. Plaques

Table 1
Slurry composition (per 100 g)

Component	Ni (g)	H_2O (g)	Cellulose (g)
Original process			
Ni	42.5		
Cellulose solution (3.7%)		55.4	2.1
Total	42.5	55.4	2.1
New process			
Ni	42.5		
H_2O		39.7	
Cellulose solution (11.8%)		15.7	2.1
Total	42.5	55.4	2.1

made by this process using the original process were found to have a similar microstructure and density to the commercial made by casting onto a substrate (see Fig. 1). We are therefore reasonably confident that horizontal tape casting does not alter the properties of the material to any significant extent and therefore offers a viable method for studying the effect of process modifications on the plaque strength.

Images of the sample surface were obtained using an ElectroScan 2020 environmental SEM. The images of the fracture surface for quantitative analysis of fracture points were obtained using Philips 515 SEM. Tensile strength measurements were conducted using an Instron 4411 load frame with loads up to 50 N. X-ray photoelectron spectroscopy analysis of sintered plaques was performed using a PHI 5500 ESCA system.

4. Results and discussion

The results of Z-potential measurements are shown in Fig. 4. The Z-potential increases rapidly with increasing

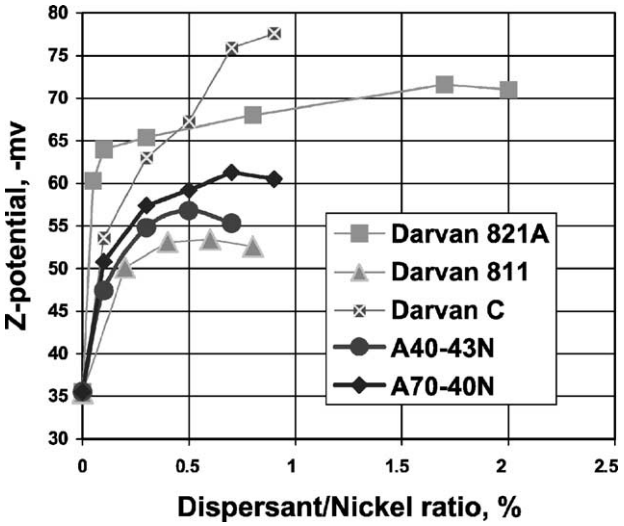
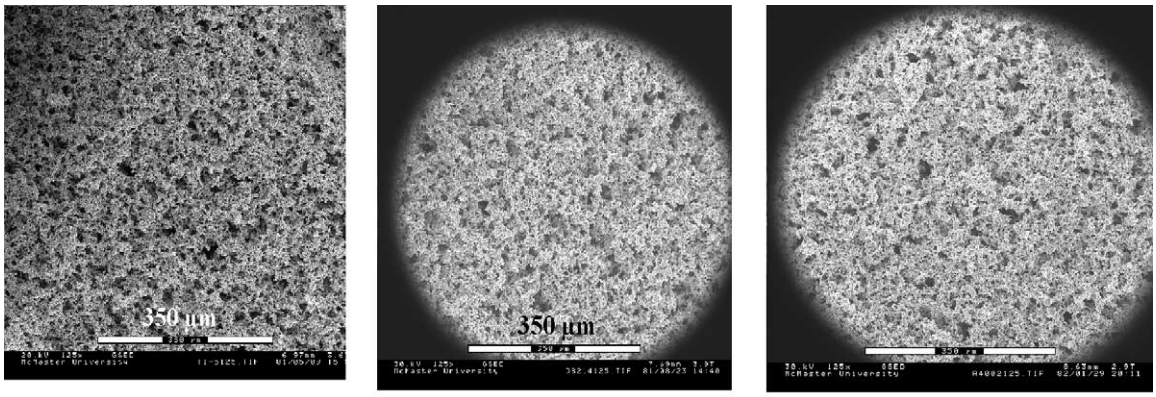


Fig. 4. The influence of different dispersants on the Z-potential of nickel powder.



(a) (b) (c)

Fig. 5. The effect of dispersants on the plaque appearance. (a) Darvan C, (b) Darvan 821A, (c) Polacrlyl A40-43N.

concentration and then levels off or even decreases. Optimum benefits can be achieved with as little as 0.1% dispersant concentration. Darvan 821A and Darvan C, based on ammonium polyacrylate, appeared to be the most effective dispersant of those studied.

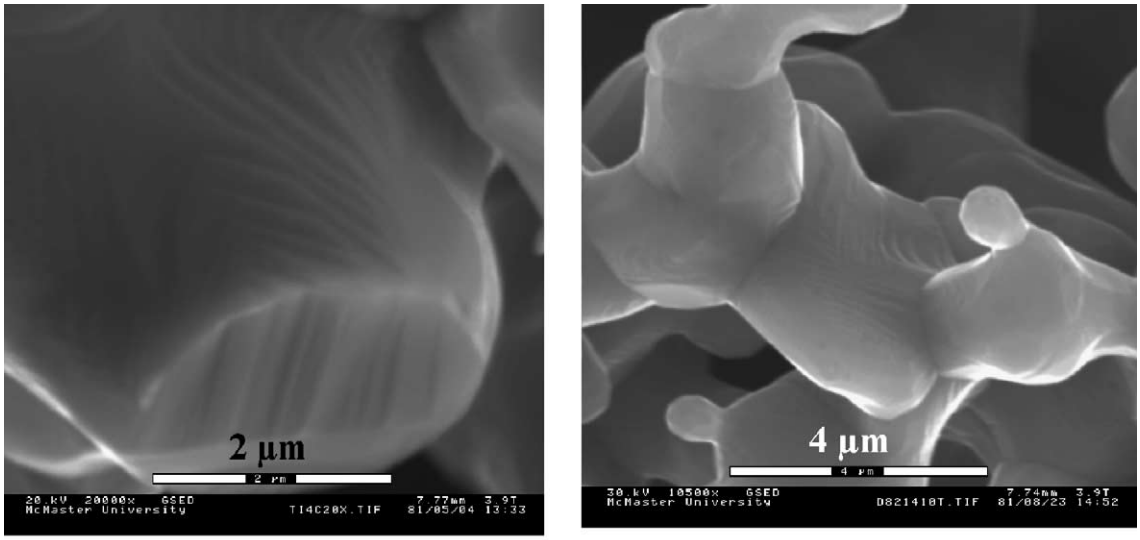
The microstructures of plaques prepared with various dispersants are shown in Fig. 5. There is a clear improvement in the microstructure in terms of better uniformity, as compared to the plaque depicted in Fig. 1. Similar results were observed with other dispersants.

Despite the observed improvement in microstructure the tensile strength exhibited by all of the plaques made using the Darvan dispersants was very low up to four times lower than that of the plaques prepared without dispersants (1.2 MPa versus 3–5 MPa). Moreover, these plaques were quite brittle.

Detailed SEM images (Fig. 6) suggested that the neck growth between nickel particles during the sintering process as well as the surface morphology of the nickel had been adversely affected by the addition of these dispersants. Fig. 6a shows that the fracture surface of the nickel filament exhibits brittle deformation. Fig. 6b indicates clearly that sintering did not occur properly as boundaries between grains are quite visible and the surface of the structure is rough. The most probable cause of such behavior was contamination of the powder surface by the dispersants as their presence was the only difference between conventional and new composition of sintered plaques.

To determine the nature of the contamination, X-ray photoelectron spectroscopy (XPS) of the surface of the powder sintered with and without dispersants was performed. The results are presented in Fig. 7.

The lower graph was obtained from a sample that contained the dispersant Darvan 821A, while the upper graph was typical of a sample processed without a dispersant. The lower graph shows the presence of sulfur in the form



(a) (b)

Fig. 6. Surfaces of sintered nickel powder particles. (a) With the use of Darvan C, (b) with the use of Darvan 821A.

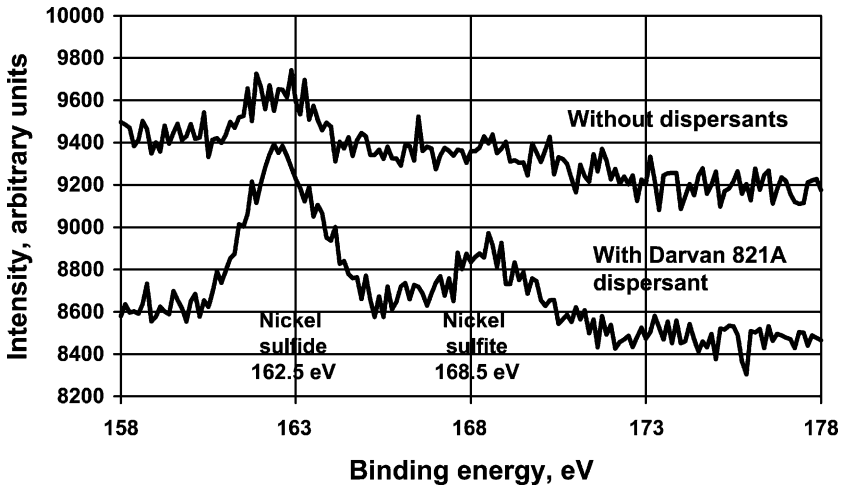


Fig. 7. The XPS data for sintered nickel powder in the range of 158–178 eV.

of sulphites (right peak) and sulphides (left peak). The sulfur-containing peaks are the only differences between samples in the entire range of binding energies. Thus, the most probable cause of the decreased material strength was the presence of sulfur that was introduced to the slurry with the dispersant. Bulk sulfur analysis of the dispersant Darvan 821A showed that it contained about 1.3% sulfur. Sulfur is commonly used to terminate the reaction and control the molecular weight in the production of many dispersants, including some of those (i.e. all of the Darvan variants) used in this study.

The tensile strength of sintered plaques that were prepared using sulfur-containing dispersants can be plotted as the function of the sulfur content. The results for Darvan 821 are shown in Fig. 8. Specific strength plotted by *Y*-axis was defined as the measured tensile strength normalized by the relative density of the plaques. In all cases we found a strong correlation, which clearly demonstrates a significant influence of sulfur on the strength of porous nickel materials, even at very low concentrations. Thus, in order to prepare a strong structure by sintering of nickel powder, sulfur contamination should be avoided.

To eliminate the influence of sulfur on the strength of a sintered nickel body, a number of sulfur-free dispersants were selected for further study. The procedure for plaque preparation remained as shown in Fig. 3. The dispersants used were Polacryl A40-43N, A70-40N and B55-50N with concentrations from 0.05 to 2% based on the weight of nickel. The tensile strength and porosity of sintered plaques is presented in Fig. 9, for plaques made both by the conventional process and for those made using the A40-43N dispersant with the modified mixing sequence. A range of porosity levels was achieved for each case by altering the sintering temperature. The results for other sulfur-free dispersants were similar. Results obtained by implementing the new mixing sequence, but without the use of any dispersant,

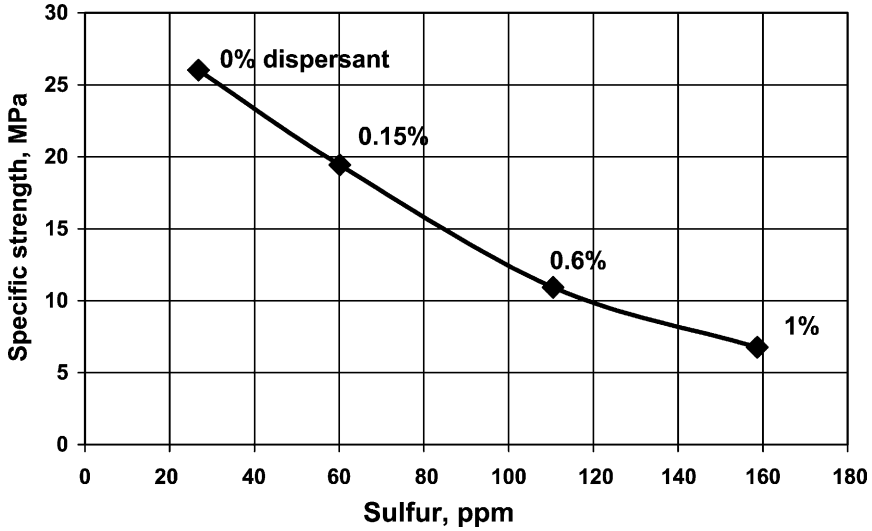


Fig. 8. Influence of sulfur on the strength of sintered nickel powder. Percentages refer to the dispersant/nickel ratio in the slurry.

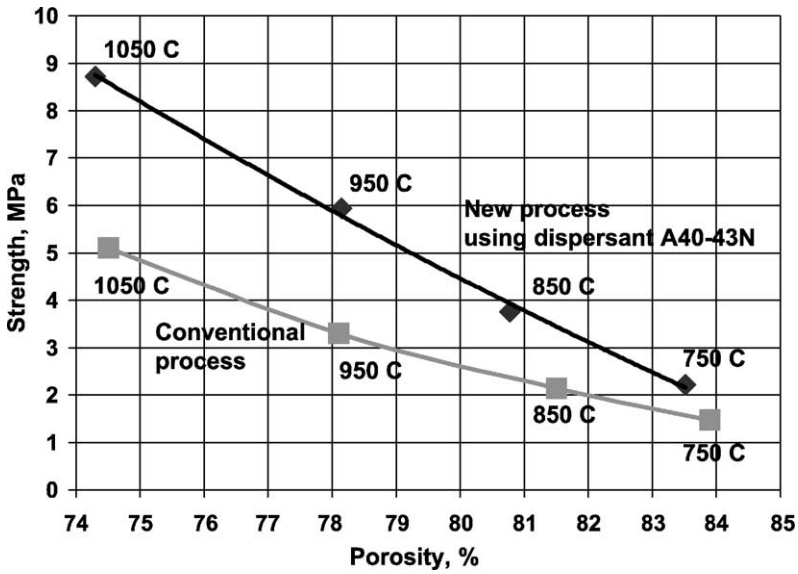


Fig. 9. Strength, porosity dependence of sintered nickel plaques. The temperatures referred to those at which the plaques were fired.

also showed considerable increase in strength in comparison to the conventional method, though slightly lower than the strength obtained using dispersants.

As can be seen, the relative increase in the strength of the plaque prepared using the new mixing sequence and sulfur-free dispersant accounts for 50–70% over the entire range of porosities studied.

A typical example of a fractured ligament is presented in Fig. 10.

In contrast to Fig. 6 the image presented in Fig. 10 shows a highly ductile fracture process, as one would expect for pure nickel. It can be noticed that during application of tensile force the neck of the filament was deformed and became thinner before the failure occurred. While this explains the strength differences observed between the plaques produced with sulfur-free dispersants and those produced using sulfur-contaminated dispersants, it does not explain the significant increase in strength over the plaques produced by the original process (for which the nickel ligaments also produced ductile failures). The most probable cause of this improvement is due to changes at the macroscopic level in the homogeneity of the particle distribution in the sintered plaque.

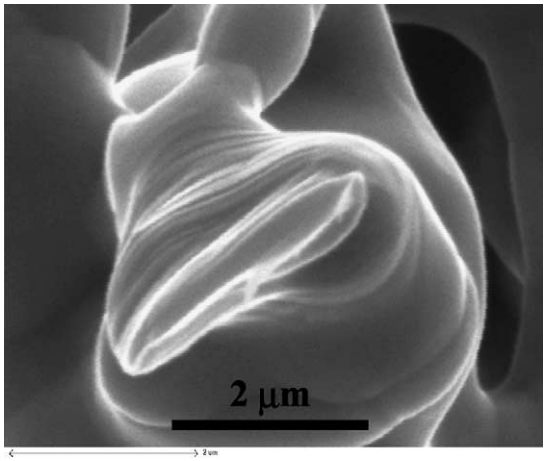


Fig. 10. The example of a fracture point.

In order to more quantitatively understand how changes in the procedure of slurry preparation affect the structure of the sintered nickel plaque and its correlation to strength increases, the fracture surfaces of several plaques were studied in detail using SEM. For each material studied about 80 images (60 μm × 60 μm each) were taken of randomly chosen areas across each fracture surface. The total areas of these images accounted for about 7.5% of the entire fracture surface. These images were processed using imaging analysis software and the total area and number of actual fracture ligaments was determined for each image. The results of measurements and calculations are shown in Table 2.

The increase in the measured strength of the plaque prepared with the new method can be understood from the higher total area of fracture ligaments (line 3) and the increased number of fractures (line 4). This data suggests that the new plaques form a more interconnected structure, which requires that more ligaments be broken as the plaque fails. Another informative number derived from the data is the area of fracture surface per fracture ligament (line 5) This number is about 1.5 times lower in the plaque prepared with the new method. It means that with the new method more ligaments resist the tensile force. From the results above and previously established tensile strengths of samples, the strength of nickel ligaments was also calculated. This appeared to be equal to 402 and 388 MPa for the conventional and modified plaque, respectively. Derived numbers correlate well with the tensile strength of pure nickel in the literature that is close to 400 MPa [5].

Table 2
Fractographic analysis

S. no.	Measured and calculated data	Conventional method	New method
1	Strength of the sample (MPa)	3.08	4.77
2	Area studied, A_t, with SEM (μm^2)	2.17×10^5	1.96×10^5
3	Percentage of the area occupied by fracture ligaments	0.766	1.23
4	Number of fracture, n_f, ligaments per mm^2	2860	4800
5	Fracture surface area per ligament (μm^2)	350	208

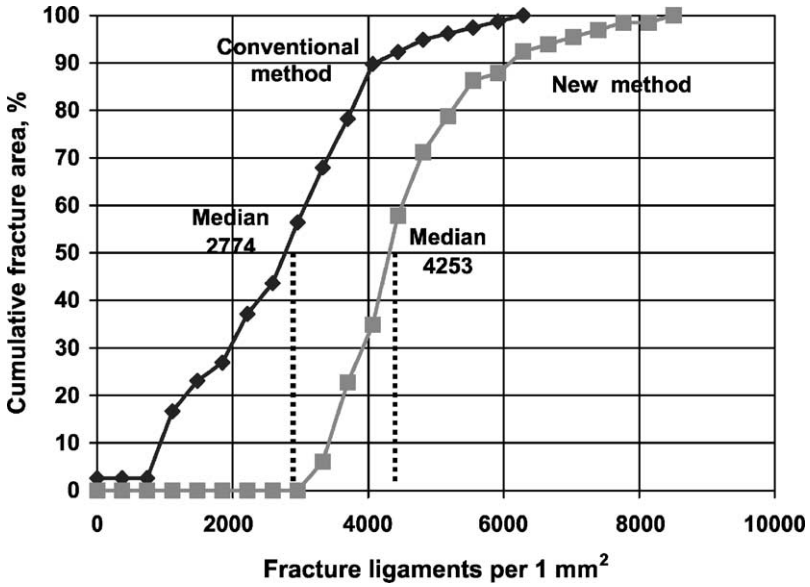


Fig. 11. Cumulative distribution of fracture points.

Another important factor in the development of the improved strength is the distribution of fracture ligaments through the area of fracture. One indication of the improved distribution is given in Fig. 9, where the porosity achieved by the new process is somewhat less for a given temperature than for the conventional process. The increase in homogeneity shown in Fig. 5 suggests that nickel ligaments have filled in the large pores. To further understand the change in ligaments distribution, the number of fracture ligaments was obtained for each sample out of about 80 images 60 μm × 60 μm. A frequency distribution based on these numbers was derived for the area of images that contained a given number of fracture ligaments. The results are expressed in the form of a cumulative distribution plot as shown in Fig. 11.

As seen from the graph, the distribution of fracture loci in the plaque prepared by the modified technique is closer to the classic Gauss distribution and it is shifted towards a larger average value. The higher median value indicates that the new processing technique results in more fractured ligaments per unit area, while the shape of the distribution is an indicator of plaque uniformity. Moreover the graph indicates a large reduction in the number of regions that contain a small density of ligaments. Indeed, the minimum ligament density is around 3000 ligaments per mm^2 for the new process, as compared to less than 1000 for the original process. The higher ligament density follows as a direct consequence of removing the large pores.

The improved uniformity leads to an increase of the plaque strength by 50–70% at the same porosity level. A strength increase of this magnitude can only occur if the interconnectivity of the particles in the plaque has increased. However, even this increased strength is around 10 times less than the strength that one would calculate based on the theory of uniform foams [6]. These sintered plaques therefore do not form a continuous, regular cellular structure. Indeed many of the particles remain unconnected over most of their length to other particles. From a mechanical perspective these ligaments are of no value. However, they still contribute electrical conductivity to the electrode; nickel filaments serve as conducting probes into the impregnated active mass. A processing method that would result in the strength to porosity ratio for these materials comparable to what one can achieve in nickel foams appears to be unlikely. However, this ratio has been demonstrated to be improved substantially through process control.

5. Conclusions

A new approach to slurry preparation has been developed in the manufacture of porous nickel plaques from filamen-

tary nickel powders. The approach primarily involves an improved sequence for the mixing of the slurry components with the appropriate use of dispersants. A better distribution of nickel powder particles in the green and sintered material has been produced. A small amount of sulfur was found to have a dramatic deleterious effect on the strength of the sintered nickel powder. Therefore, only sulfur-free chemicals should be used in processing these materials. Through a combination of the new technique of slurry preparation and the selection of sulfur-free dispersants, the strength to porosity ratio of sintered nickel plaques was increased. Analysis of fracture surfaces has been used to quantify the effect of the new process in terms of increased uniformity of the ligament spacing and increased density of connected ligaments.

References

[1] V.A. Ettel, New materials for NiCad batteries, in: Proceedings of the Paper Presentation at Nickel-Cadmium Battery Conference NiCad 96 of the International Cadmium Association, NiCad 96, Barcelona, Spain, 30 September–3 October 1996.
[2] V.A. Tracey, Nickel powders into sintered structures for the alkaline battery: porosity studies, Ind. Eng. Chem. Prod. Res. Dev. 25 (4) (1986) 582.
[3] G.D. Parfitt, Dispersion of Powders in Liquids, Applied Science Publishers Ltd., London, 1973, pp. 1–43.
[4] D.W. Richerson, Modern Ceramic Engineering, Marcel Dekker, New York, 1982, p. 191.
[5] W. Betteridge, Nickel and its Alloys, Ellis Horwood, Chichester, UK, 1984, pp. 68–69.
[6] L.J. Gibson, M.F. Ashby, Cellular Solids: Structure and Properties, Cambridge University Press, Cambridge, 1988.