AN ESTIMATION OF THE MECHANICAL STRESS IN NICKEL ELECTRODE SINTER AND ITS IMPLICATIONS FOR NICKEL ELECTRODE CONSTRUCTION

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Summary

The mechanical stresses existing in the sinter of nickel electrodes are estimated by comparing the deterioration of the electrode during cycling with nickel fatigue data. The results indicate that at least 30% of the sinter is subject to work hardening prior to failure by fatigue. Ten per cent. of the sinter is stressed at substantially higher levels than the remainder and fails within 200 discharge cycles It is suggested that a nickel alloy that has less severe work hardening characteristics would benefit the electrode's cycling behavior. Also, the incorporation of a "Shear free" current collector into the electrode is suggested as a means of extending cycle life.

Introduction

The calculation of the mechanical stresses that exist in sintered nickel electrodes is made difficult by the random, microscopic nature of the structure, and by our ignorance of the elastic properties of the electrochemically active materials ($Ni(OH)_2$, NiOOH and mixtures thereof [1]) Gross estimated the stresses could reach 1.1×10^8 Pa in small pores of the structure due to the gas pressure that can be generated on overcharge [2]. However, an estimation of the stresses that exist in the electrode due to active material molar volume changes has not, to this author's knowledge, been previously done

In this paper a model, based on fatigue failure of the nickel sinter [3], developed to describe the relationship between electrode conductivity and electrode capacity, is used as the basis of comparison between the electrode's deterioration and nickel fatigue data. The model is statistical in nature, which transforms the microscopic sinter element problem to a structurally macroscopic one. This transformation allows the maximum stresses to be estimated

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Theoretical

Consider a mechanically isotropic electrode, on a macroscopic scale, that is composed of randomly orientated, electrically connected, strands of nickel sinter Each sinter strand will have an individual geometry, conductivity, and electrochemical capacity (due to impregnated active material) As the electrode is cycled the active material molar volume changes will cause corresponding mechanical strains in the sintered elements which are unique to that element. The types of cyclic stress applied to the elements can be longitudinal, transverse, torsional, or combinations thereof. A stress analysis of a single element would, in general, be very complex and would require estimates of the active material elastic properties, data which are currently not available The approach used here is statistical in nature and assumes that only longitudinal strains exist in the sinter, this allows the above difficulties to be ignored The theoretical treatment of the nickel sinter is given in detail in ref 4. A brief outline is presented here

To treat the nickel sinter theoretically, a continuous probability distribution function, f, is defined as follows

$$f = \frac{1}{N} \frac{dn}{dc}$$

where n is the number of singly broken sinter elements, N is the total number of elements, and c is the number of charge/discharge cycles n is thus given by

$$n = N \int_0^c f \, dz$$

Let g be the conductivity of each element and, assuming the elements are connected in a series–parallel circuit *ad infinitum*, the uncycled sinter conductivity, G_0, is given by

$$G_0 = gN^{1/3}$$

The normalized, cycled sinter conductivity, G/G_0, is given by

$$G/G_0 = 1 - \left(\int_0^c f \, dz \right)^{2/3}$$

rearranging

$$\int_0^c f \, dz = (1 - G/G_0)^{3/2} \tag{1}$$

Equation (1) gives the accumulated ratio of singly fractured sinter elements to the total number of elements as a function of cycles.

The relationship between cyclic plastic strain, $\Delta\epsilon_p$ and stress cycles, ψ, is well known and is given by

$$\psi^{\beta} \Delta\epsilon_p = K \qquad (2)$$

Where β and K are constants of the material being fatigued Coffin and Tavernelli have done extensive fatigue testing of annealed Nickel A [5, 6], and the properties of this material are assumed to be identical to that of the nickel sinter For Nickel A, β and K are given by 0.575 and 1.06, respectively These fatigue data are for an alternating compressive–tensile load profile and do not allow for fatigue in bending or torsion, which will undoubtedly exist within the sinter. Thus, the results reported herein have to be viewed as qualitative with respect to absolute stress values.

It is normal practice to assume that the stress–strain relationships are symmetric with respect to compression–tension loading. In ref. 5 it is pointed out that eqn. (2) is valid for the simple tension case or the reported-upon compression–tension cycling regime. In this paper the initial discharged state of the electrode is assumed to correspond to the initial zero stress state of the fatigue test sample Therefore, each electrode discharge cycle corresponds to one-half fatigue load cycle, *i e* , $\psi = 2c$.

Equations (1) and (2), plus the experimental fatigue data, provide the basis for the stress estimations reported herein

Experimental

The experimental electrode was made from plaque that did not contain a current collector. The current collector was eliminated so that the substrate structure was macroscopically isotropic and would provide reasonable correlation with theory The electrode measured 1 mm × 12.7 mm × 78.9 mm and was tabbed at each end so that *in situ* resistance measurements could be made The resistance was continuously monitored by a Hewlett-Packard model 4328A milliohmeter connected to a strip chart recorder The current to each electrode tab was equalized by the use of precision resistors. This eliminated any possible voltage bias instrumentational problems.

In making these resistance measurements it is assumed that the electronically conductive material is the nickel sinter and any contribution by the electrochemically active materials is negligible.

The plaque was loaded using the electrochemical process described in ref. 7 No stress-modifying additives such as $Co(NO_3)_2$ were used in the impregnation process so as to accelerate the electrode fatigue [7]. The electrode was loaded to 1.62 g/cm^3 void, measured after the completion of three formation cycles. The electrode was cycled at the 1.25 *C* rate (assuming a one electron exchange) It was charged for one hour and subsequently discharged to 0.4 V *vs.* cadmium counter electrodes. Thus, the cycling was between 25% overcharge and 100% depth of discharge.

The Nickel A experimental fatigue data were taken from ref. 5

Results

The cyclıng results of an electrode are shown ın Fıg. 1, where the plotted utılızatıon effıcıency ıs the ratıo of actual capacıty to ıts theoretıcal value In ref. 4 an equatıon ıs derıved that relates a sıntered electrode's conductıvıty to ıts capacıty. The capacıty predıcted from thıs relatıonshıp, based on the observed conductıvıty, ıs shown as the dashed lıne ın Fıg 1. Note that the capacıty of the electrode declines markedly from that predıcted after about the 700th dıscharge cycle. Thıs decline ıs due to an unknown cause that ıs apparently unrelated to fatıgue faılure of the sınter [4]. Test data from several other electrodes ın thıs work show very sımılar behavıor In thıs paper, thıs devıatıon ıs ıgnored as the conductıvıty ratıo, G/G_0, mo-

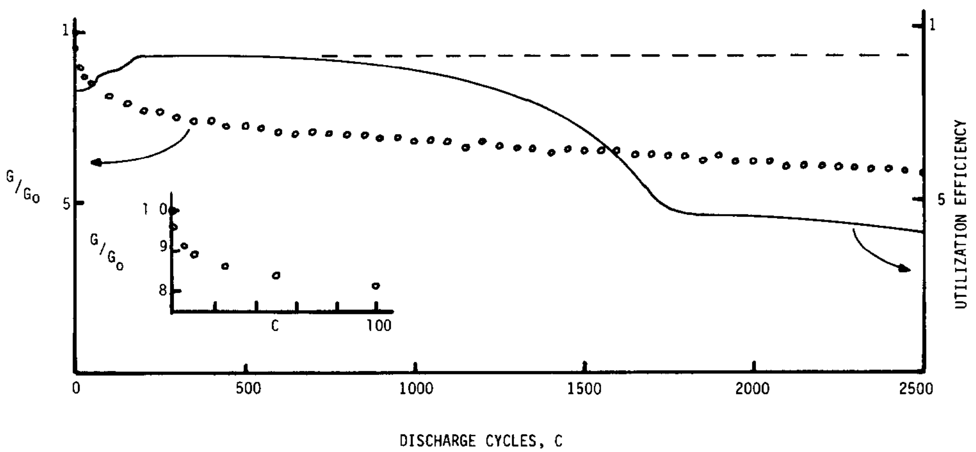

Fıg 1 The cyclıng behavior of the gridless electrode used for stress analysıs

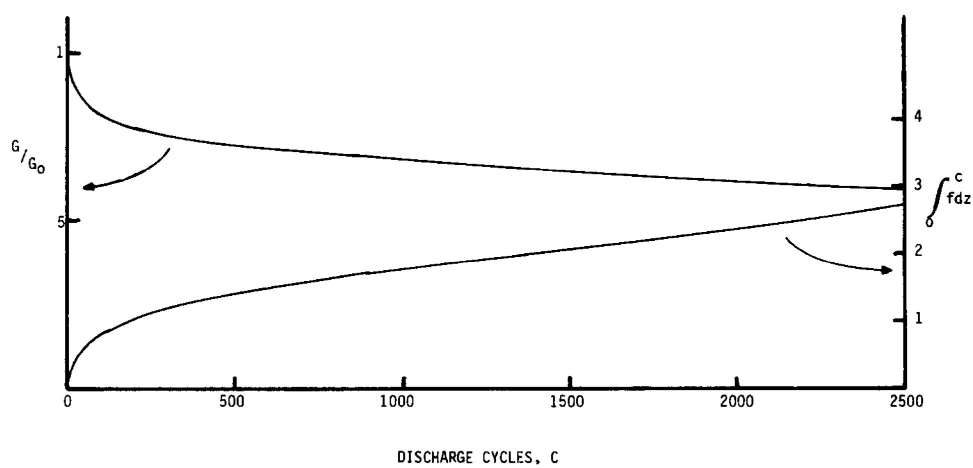

Fıg 2 Fractıon of sıngly broken elements *vs* discharge cycles

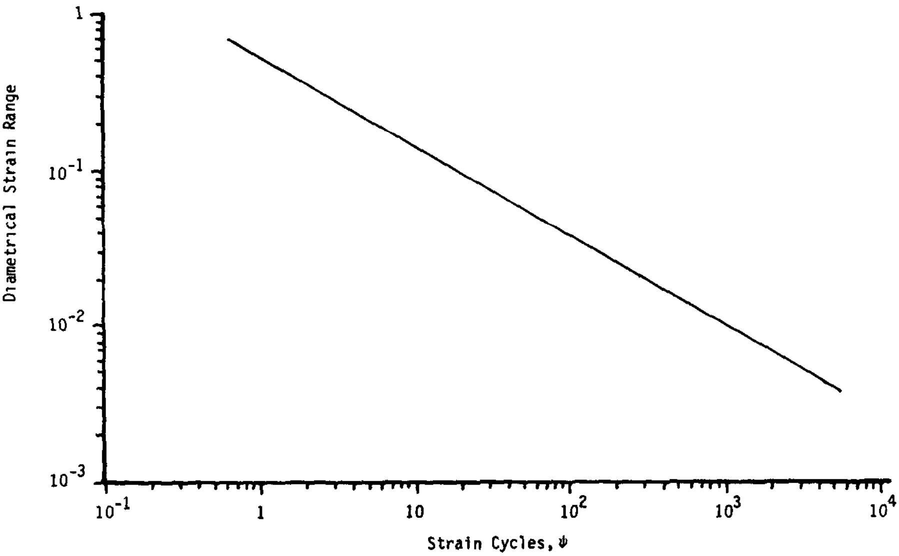

Fig 3 Diametrical strain range *vs* cycles to failure — Nickel A annealed, adapted from Coffin and Tavernelli, by permission

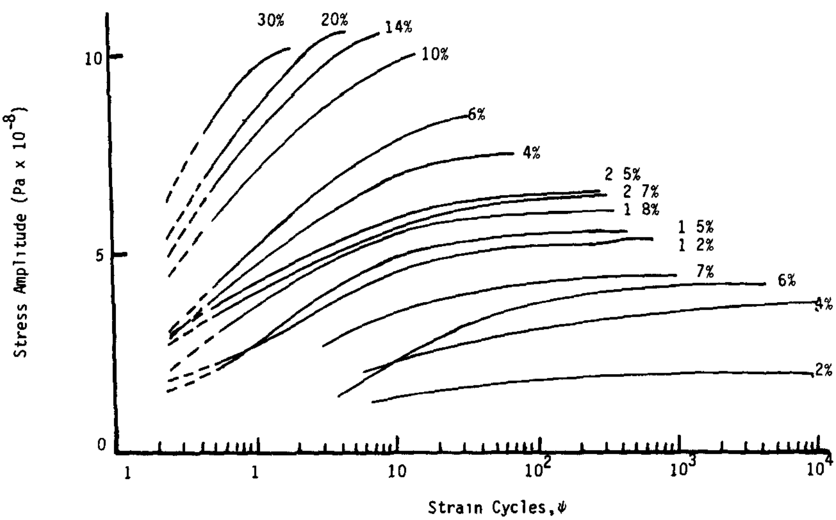

Fig 4 Stress amplitude *vs* strain cycles — Nickel A annealed, from Coffin and Tavernelli, by permission

notonically decreases in a well behaved manner This point will be discussed more fully later. In Fig. 2 the conductivity data are shown in smoothed form along with the integral of the distribution function which is calculated from eqn. (1).

In Figures 3 and 4 data from ref. 5 are presented. These data describe the "large strain" fatigue characteristics of Nickel A when subjected to a compression/tension load cycle regime. The data for each curve of Fig. 4 are for a constant diametrical strain range, $\Delta\epsilon_d$ The test samples were of the large radius, notched type characteristic of metallurgical fatigue samples, with the test section diameters being nominally 0.64 cm.

Figure 3 is a plot of eqn (2) except that the diametrical strain range has been substituted for the longitudinal plastic-strain range which differs by a factor of two

Similarly, in Fig 4 the stresses of ref. 5 are divided by two to represent a stress amplitude rather than a stress range. This corresponds to the previous comments concerning the compression–tension loading of the fatigue samples

Discussion

To estimate the level of stresses existing in the nickel sinter elements, two assumptions have to be made The first of these is that the elements are stressed in a compressive–tension longitudinal mode only. As discussed earlier, this is undoubtedly not the case, but the error introduced by this assumption is probably within the variation normally found in fatigue data, as it is sensitive to surface finish, heat treatment, etc

The second assumption is that for each sinter element there is a characteristic and constant $\Delta\epsilon_d$. This assumption implies that the element is subject to constant molar volume changes of active material and that the active material does not shed throughout the element's cycle life. In Fig. 1 the deviation of the capacity from that predicted (the previously mentioned capacity loss) may indicate that this assumption is not valid beyond the 700th discharge cycle. However, if there is a significant $\Delta\epsilon_d$ change, one would expect to observe a corresponding change in the conductivity behavior. Such a change is not observed, therefore the assumption will be treated as reasonable for all the cyclic testing.

Combining the results of Figs. 2 and 3 a $\Delta\epsilon_d$ can be associated with each value of $\int_0^c f\,dz$, *i.e* , the sinter elements that fail at a given cycle by fatigue have been subjected to a characteristic mechanical strain that corresponds with the fatigue failure data. From Fig. 4, each value of $\Delta\epsilon_d$ results in a different stress *vs.* cycle profile Figure 4 also shows that Nickel A work hardens significantly before failing in fatigue. The quarter cycle data of this Figure is the first peak stress point in the cycle testing and this corresponds to the end of the first charge cycle of the electrode. That is, a complete molar volume change in the active materials has occurred.

With the above consideration, the data of Figs. 2, 3, and 4 are readily combined to obtain Fig. 5. Figure 5 shows the estimated stresses existing in the nickel sinter both as a function of singly broken elements and of discharge cycles. The most important features of this Figure are that nominally 10% of the sinter is stressed significantly above the norm and most of this sinter suffers at least a single break by 200 cycles. Additionally, the sinter work hardens throughout its cycle life.

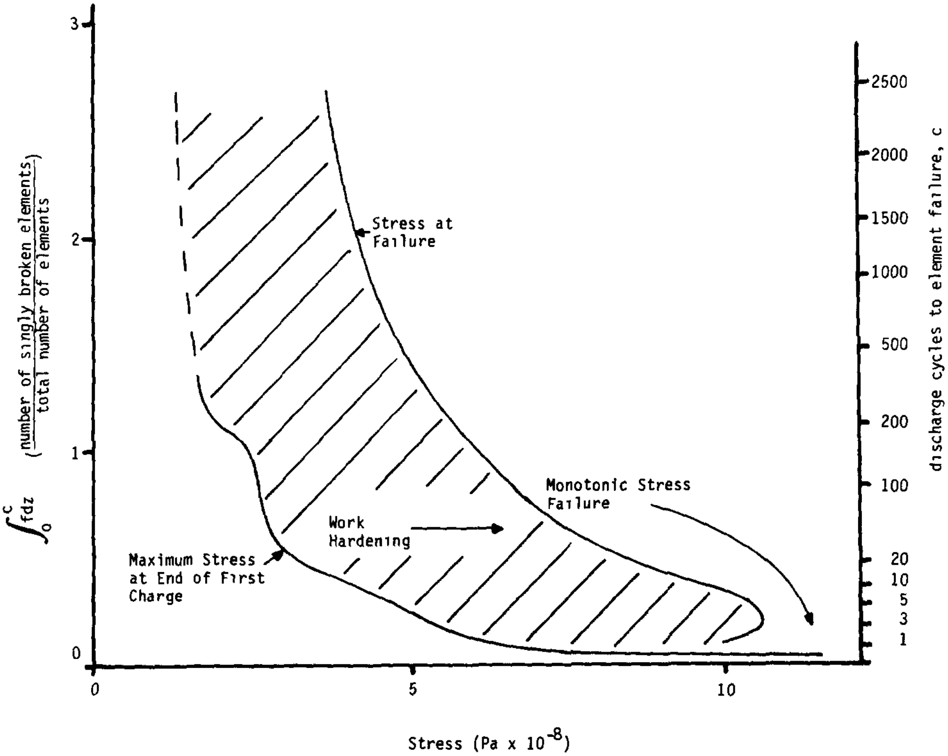

Fig 5 Distribution of maximum stresses in nickel sinter

In ref. 8 we reported that plaque hardness may be an important parameter with respect to an electrode losing capacity *via* active material shedding. It is thought that "harder" plaque will experience higher shedding rates due to increased interfacial stresses that would exist between the sinter and active material for a given molar volume change. In the light of Fig. 5, plaque hardness is a variable quantity due to work hardening. Thus, starting with a soft plaque probably delays shedding, but as the electrode cycles it work hardens with a corresponding increase in, the interfacial stresses, so that shedding may ultimately become severe This observation suggests that a substrate material that work hardens at a lower rate may be desirable. The nickel alloy Inconel 718 may be an interesting candidate as a nickel substitute in this regard.

Another area where stress reduction improvements in the nickel electrode structure seem worthwhile is the form of the current collector. In previously reported work [9] it was shown that sinter electrodes with conventional current collectors have a high shear stress region at the sinter–collector interface. The sinter fracture rate in this region is greatly accelerated due to the mechanical anisotropy introduced by the current collector. These regions of high shear failure result in macropores being formed which, in turn, are a cause of electrode blistering. To avoid this failure mode a

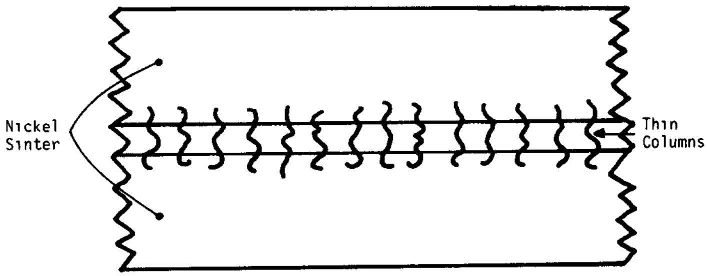

Fig 6 Idealized electrode structure to eliminate shear stresses at current collection grid

current collector must be used which reduces the shear stresses In Fig 6 an idealized sketch of an electrode with a modified current collector is shown This electrode can be viewed as two gridless electrodes connected by thin columns. It is apparent that the electrode can grow uniformly along its length and width without experiencing shear stresses due to a current collector. Electrodes with current collector structures approximating the above ideal are being fabricated in this laboratory and will be reported upon in a future communication

Conclusions

In summary, a technique for estimating the stresses in nickel electrode sinter was introduced The stress estimations yielded several interesting results. (i) approximately 10% of the sinter is stressed at a substantially higher level than the remainder; (ii) the stress levels are high enough to cause significant work hardening of the sinter, possibly enhancing active material shedding, (iii) it may be worthwhile investigating other substrate materials that have a lower work hardening sensitivity.

It was also concluded that electrode stresses could be reduced by incorporating a "shear free" current collector into the electrode. It is thought that such a current collector will alleviate many of the reported blistering problems associated with nickel electrodes.

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Figure 6 was originally presented at the Fall, 1983, Meeting of the Electrochemical Society, Inc held in Washington, DC

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