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Report

THE PREPARATION AND PROPERTIES OF SINTERED Nb_3Sn

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THE PREPARATION AND PROPERTIES OF SINTERED Nb_3Sn

by

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ABSTRACT

Sintered Nb_3Sn has been formed, which is capable of supporting current densities greater than 10^5 amps/cm^2 at 50 kG, and is stable against field changes of at least 55 kG. The factors which affect stability are discussed, including the importance of the structure of the sintered material.

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1. INTRODUCTION

The intermetallic compound Nb_3Sn is a superconductor with a transition temperature of $18^{\circ}K$ and upper critical field about 200 kG. In 1961 Kunzler(1) showed it to be capable of carrying current densities greater than $10^5 A/cm^2$ in a magnetic field of 88 kG. Two coils using Nb_3Sn conductors have recently been operated at 100 kG. For these reasons it is a promising material for the production of high field solenoids and already it is available commercially in five different forms.

A major difficulty in using Nb_3Sn is that it is a very brittle material requiring careful mechanical handling. Thus the material must either be used in the form of a film of only a few microns thickness in which case it is sufficiently flexible for coil winding, or in a thicker wire in which case the compound must be formed in situ by a high temperature reaction yielding a coil which cannot be unwound for repair or modification. In either case the necessary processing of the material even before it is wound into a coil is expensive, and the presently available commercial materials cost about £2,000 per lb of superconductor, compared with £12 per lb for the basic materials.

The high cost of processing Nb_3Sn wire has led to considerable interest in devising cheaper ways of forming and using the compound. Since the cheapest form of niobium is the powder, an obvious approach is direct sintering of niobium and tin powders. Reaction occurs at about $1,000^{\circ}C$ and it only requires a few hours at this temperature to form the compound(2,3).

Because of its simplicity, this approach has been widely investigated. It suffers, however, from two serious disadvantages, both of which stem from the fact that with this process it is not possible to make specimens of small cross-section. First, in order to use the whole cross-section of the material, it is necessary for magnetic flux to diffuse through the material and this is an unstable process which may result in quenching of the superconductor(4). Secondly, if reasonable current densities are achieved in a coil of this form, the total current which must be supplied will be above 10,000 amps, and this introduces serious problems in energising the coil.

While both of these problems need to be solved before coils can be constructed from sintered Nb_3Sn, it appears sensible to demonstrate that a material capable of carrying a high current density and free from instabilities can be formed before attempting the problem of fabricating and supplying current to a coil. It will be shown in this report that a stable material has been developed.

2. PRELIMINARY EXPERIMENTS

Although basically simple, there are a large number of parameters which may be varied in the process of sintering compressed niobium and tin powders. Thus the proportion of the two constituents, the compacting pressure and the time and temperature of sintering must be established, as well as the importance of the preparation and purity of the starting materials and the method of sintering. Preliminary experiments were therefore undertaken to show which, if any, of these were of critical importance.

In these early experiments, the only criterion was the magnetic field which could be screened by a ring before flux jumping or quenching occurred. Measurements were performed at 4.2°K, and rings of 2.0 cm O.D., 1.4 cm I.D. and about 0.7 cm long were tested in a field which increased at a rate of 40 gauss/sec up to a maximum of 55 kG. The flux density at the outer surface of the rings was measured by means of copper magnetoresistance probes.

SINTERING METHOD

Three methods of sintering the compacted powders have been used:-

(a) Sintering in a bath of liquid tin

This allows sintering to be undertaken in an open furnace since oxidation of the surface of the tin bath does not affect the compact. A high density of Nb_3Sn may also be achieved in this way since a compact of niobium powder on its own can be used, allowing the tin to enter the porous structure from the bath.(5) The major disadvantage is the lack of control of the tin content of the reacted solid.

(b) Sintering in a vacuum

In this case there may be some loss of tin by evaporation or contamination of the niobium by oxidation if the vacuum is poor. Even with a high pumping speed it was found difficult to prevent the pressure rising to 10^{-3} torr in the early stages of heating, but a pressure of 10^{-6} torr was maintained during sintering.

(c) Sintering in an inert atmosphere

In this case there will be little gain or loss of tin, but oxidation may still be a problem. 99.995% pure argon was used which was passed over Titanium at 1,000°C before reaching the compacted rings.

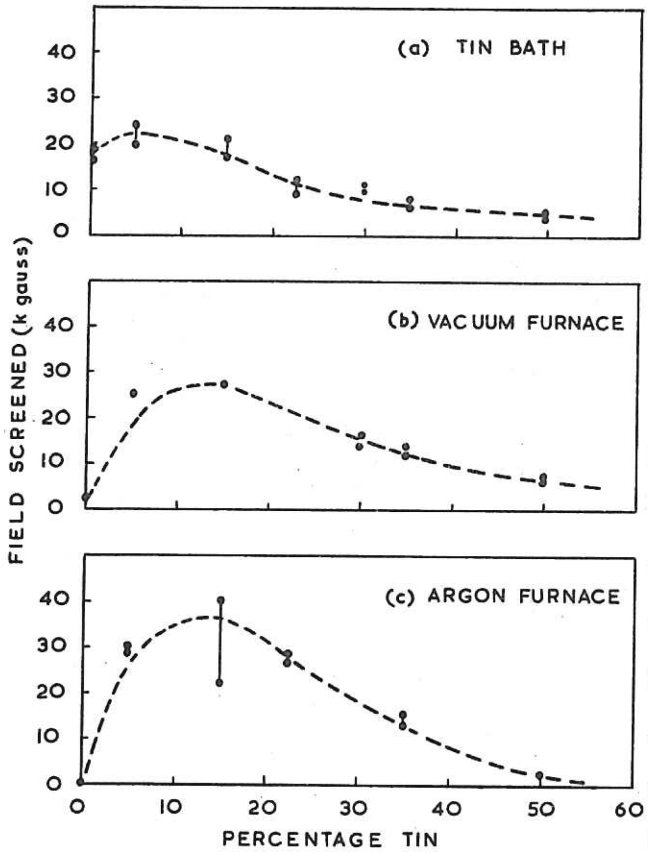

Fig. 1 (CLM-R43)
Variation of screened field with the proportion of tin in the compacted powders for three methods of sintering

Results using these three methods will be quoted in the following section, but it may be stated here that sintering in an argon atmosphere proved in practice to be the most convenient method.

COMPOSITION OF THE COMPACT

Although 25 $^{a}/_{o}$ of tin is required for the stoichiometric compound, the proportion of niobium and tin used in the compact before sintering will depend on the loss or gain of tin during processing. The effect of varying the proportion of tin over a wide range is shown in Fig.1. For material sintered in a tin bath, the best result is obtained with very little tin in the compact, sufficient being supplied from the bath. Higher screening fields were obtained with the other two methods, the best results being with about 15 $^{a}/_{o}$ tin in the compact, suggesting that either not all of the niobium reacts or that a niobium-rich compound has better superconducting properties. In neither case, however, is the initial proportion of tin found to be a critical paramater.

STARTING MATERIALS AND COMPACTING PRESSURE

Niobium powder is available from several sources in a variety of grades. Rings were made from a number of powders and their average screening fields

TABLE I

Niobium Powder	Field Screened kG
Source 1	
(a) 99.8% purity, nominally - 300 mesh	22-27
(b) as (a) but hydrogen reduced and jaw crushed	0-6
(c) as (b) but ball milled to - 150 mesh	23-28
(d) as (c) but degassed	22-29
Source 2	
(a) Dendritic powder 99.7% purity, 2000 micron size	0-8
(b) Fine powder 99.6% purity, nominally -300 mesh	20-24

are shown in Table I. In all cases 15 $^{a}/o$ of 99.9% pure tin powder of -325 mesh size was used, the powders were pressed at 70,000 psi and sintered in an argon atmosphere. All the results are seen to be comparable except for the two largest particle sizes. Using Niobium Powder 1(d) (see Table I), compacts were formed at four pressures, sintered and tested. The results are shown in Table II and show a slight increase in screening field with pressure.

TABLE II

Compacting pressure psi x 10^{-3}	Field Screened kG
45	23
90	26
135	28
180	31

CONCLUSIONS FROM PRELIMINARY EXPERIMENTS

The screening fields obtained did not appear to depend critically upon any of the parameters studied. In addition to the results already quoted, both the temperature and the time of sintering have been varied over limited ranges without significant effect. The optimum appeared to be niobium powder 1(d) compressed with 15 $^{a}/o$ tin, sintered for two hours at 980°C in an argon furnace. With these conditions rings were obtained capable of screening fields of 25 to 30 kG, but the results were not consistent.

3. EXPERIMENTS WITH FINE POWDERS

In 1964 Goldsmid and Corsan(6) published some results of their study of sintered Nb_3Sn in which they had screened fields up to 50 kG. An important feature of their rings was that the average density was only 4.5 grams/cm^3 compared with 6.5 grams/cm^3 for the rings described in the previous section. It was suggested that the importance of the low density was that it facilitated cooling of the ring but no indication was given as to how the rings were prepared.

THE EFFECT OF POROSITY

In an effort to reduce the average density of rings, the niobium and tin powders were pressed with a variety of fillers such as nitro-cellulose, which either decomposed or were sufficiently volatile to evaporate during sintering. These methods resulted, however, in rings of low mechanical strength without improved performance. Further experiments were therefore undertaken in which the porosity was varied by changing the compacting pressure. Rings were made and tested as before except that a new batch of niobium powder, similar to 1(a) was used, the mixing of the powders was improved, and niobium was used as a getter in the furnace instead of titanium. The results are summarised in Table III.

TABLE III

Compacting pressure psi x 10^{-3}	Average density grams/cm^3	Field screened kG
22.5	4.4	47
45	5.1	51
90	6.1	55

The most striking result in Table III is that the field which can be screened appears to increase with increasing density. It has been subsequently demonstrated, however, that this is actually due to the fact that the current density carried by the material increases with pressure. Thus, the rings pressed at 22,500 and 45,000 psi both quenched when the whole cross-section of the ring was carrying current. This corresponds to a current density of 1.5×10^5 A/cm^2 at 50 kG in the 45,000 psi ring, compared with a value of 3.6×10^4 A/cm^2 obtained by Goldsmid and Corsan.

The results in Table III also show that very low densities are not necessary for good stability. It will be shown later that it is the distribution of porosity which is important, rather than its average value. This is borne out by the fact that at higher compacting pressures extremely erratic results were obtained. Not only were there large variations in the screened field from one ring to another, but consecutive tests on a given ring often produced results differing by a factor of 2 to 1. Improved results were obtained with these rings by waiting for a period of one hour between tests and this suggests that a considerable time was necessary for liquid helium to diffuse into the porous structure in these cases. At compacting pressures below 90,000 psi no such effects were observed and consistent results were obtained in tests at two-minute intervals. It may be noted that Corsan(7), using a pressure of only 56,000 psi, had to wait two hours between tests to obtain reproducible results.

THE EFFECT OF PARTICLE SIZE

If the distribution of porosity is important in obtaining a stable material, the particle size of the initial powders is obviously also important. The niobium powders 1(a) and 1(d) and the tin powder were all sieved and graded and the distribution of particle size is shown in Table IV.

TABLE IV

Sieve size	Particle size (Microns)	Percentage by Weight		
		Nb 1(a)	Nb 1(d)	Sn
> - 150	> 104	0	2.2	4.9
-150 to -200	104 to 76	1.3	13.2	17.0
-200 to -240	76 to 63	1.3	16.5	11.2
240 to 300	63 to 53	60.8	12.1	4.1
< -300	< 53	36.6	56.0	62.8

In each case it is seen that there is a proportion which is above the specified size. Rings were therefore made with niobium of varying particle sizes obtained from the niobium powder 1(d) compacted at 45,000 psi with the finest grade of tin. Results are shown in Table V.

The results show that the screened field increases as the niobium particle size is decreased. It has again been found that in all cases except -300 mesh niobium powder the screened field is limited by the current density, thus indicating that current density is increasing as particle size decreases.

TABLE V

Nb Particle size (microns)	Field screened (kG)
104 - 76	28
76 - 63	34
63 - 53	40
< 53	45

TABLE VI

Rate of rise of field (gauss/sec)	Field screened kG	
	Nb 1(a)	Nb 1(d)
40	> 55*	≈ 45
80	> 55*	39 - 42
220	40 - 42	29 - 33

*Limited by field available

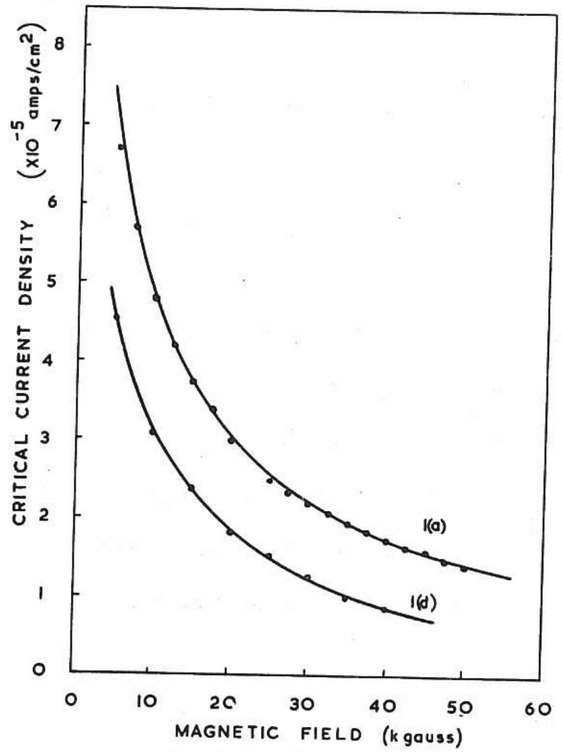

Fig. 2 (CLM-R 43)
Critical current density as a function of local field for sintered Nb_3Sn made from Niobium powders 1(a) and 1(d) sieved to less than -300 mesh

The results in Table V, although indicating how the current density of the material may be improved, do not give any indication of the limit of stability of the material against flux jumping. To do this, solid cylinders instead of hollow cylinders were made, having the same outside diameter and length as the rings previously tested. Niobium powders of type 1(a) and 1(d) sieved to less then -300 mesh were used and results are shown in Table VI for three different rates of rise of the field. It is seen that the powder from source 1(a) is noticeably better than the other and that when tested with the field rising at a rate of 40 gauss/sec and 80 gauss/sec, its limit of stability was greater than 55 kG which was the maximum field available.

CURRENT DENSITY

The flux diffusing into the rings can be measured with a search coil and the current density in the material calculated by means of the critical state model. The results for rings made with niobium powders sieved to less than -300 mesh are shown in Fig.2, and these were reproducible for several rings. For comparison, the result for material made with niobium powder 1(a) is also shown in Fig. 3 together with published average current densities for short samples of four commercially available Nb_3Sn wires or tapes.

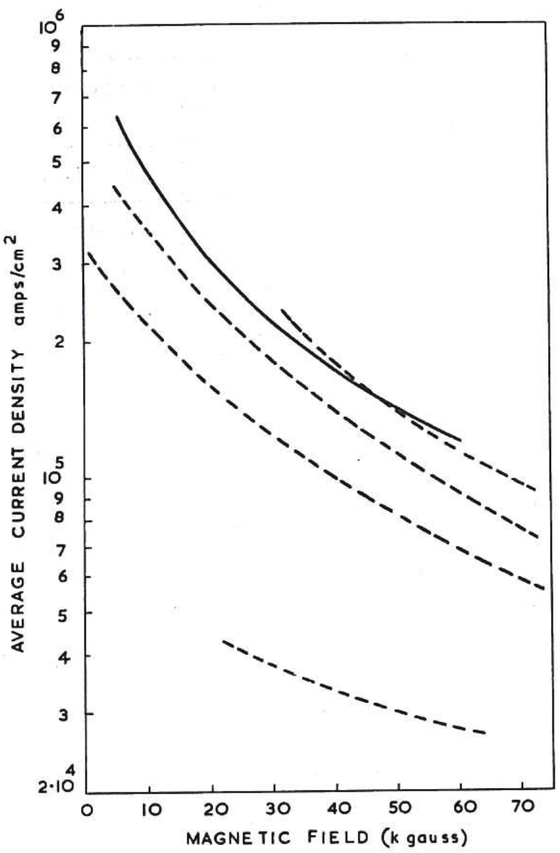

Fig. 3 (CLM-R 43)
Critical current density as a function of local field for sintered Nb_3Sn made from Niobium powder 1(a) sieved to less than -300 mesh (solid line), compared with the average current densities of four commercially available Nb_3Sn wires and tapes (dotted lines)

4. THE LIMIT OF STABILITY

To understand the results outlined above, it is desirable to enquire further into the mechanism of flux jumping and quenching. Experimentally it is observed that in a ring which is screening a high field the flux enters in small jumps and thus the material must be able to absorb the energy associated with these jumps without quenching. A simple limit of stability may be obtained by balancing the energy dissipated by a small flux jump against the thermal energy which can be absorbed instantaneously by the material.

STABILITY CRITERION

The current density at any point in a superconductor is a function of the local magnetic field and temperature. Its dependence upon the local field, H, may be approximated by

$$J = \frac{J_o H_o}{H + H_o}$$

where J_o and H_o are constants. (For the curve 1(a) of Fig.2, $J_o = 1.2 \times 10^6$ amps/cm², $H_o = 3$ kG).

The total depth of penetration, Δ, for a field H_s at the surface of a semi-infinite block of superconductor is

$$\Delta = (H_s^2 + 2 H_s H_o) / 8 \pi J_o H_o$$

and the field at a depth $(\Delta - x)$ from the surface is

$$H_x = \sqrt{H_o^2 + 8 \pi J_o H_o x} - H_o$$

If the surface field changes by δH, the total flux moving past a plane at $(\Delta - x)$ is

$$\delta\Phi = \frac{(H_o + H_s)(\sqrt{1 + 8\pi J_o x/H_o} - 1)}{4\pi J_o} \delta H$$

and the energy dissipated by the change is

$$\delta E = \frac{(H_o + H_s)(\sqrt{1 + 8\pi J_o x/H_o} - 1)}{4\pi\sqrt{1 + 8\pi J \;\; x/H}} \delta$$

If this energy is dissipated in a time which is short compared with the thermal time constant of the material $(\tau = \frac{s \rho \Delta^2}{K})$, the local temperature will increase, reducing the current density by

$$\delta J = \frac{J_o (H_0 + H_s)(\sqrt{1 + 8\pi J_o x/H_o} - 1)}{4\pi s \rho T_o(1 + 8\pi J \;\; x/H_o}$$

where T_o is a characteristic temperature (defined by $J/T_o = dJ/dT$) which is less than the critical temperature of the superconductor.

Integrating over the depth of penetration, the total change of current represents a change of surface field

$$\delta H' = - \frac{(H_o + H_s) H_o}{4\pi s \rho T_o} \left\{ \frac{H_s}{H_o} - \ln \left(\frac{H_s + H_o}{H_o} \right) \right\} \delta H$$

A rough criterion of stability is that this resultant change $\delta H'$ should not exceed the initial change δH, i.e.

$$\frac{(H_o + H_s) H_o}{4\pi s \rho T_o} \left\{ \frac{H_s}{H_o} - \ln \left(\frac{H_s + H_o}{H_o} \right) \right\} \leqslant 1$$

If $H_s \gg H_0$, which would be true in any usable material, this reduces to the simple criterion

$$H_s \leqslant \sqrt{4\pi s \rho T_o}$$

This criterion is only approximate. On the one hand it neglects the fact that with a steadily increasing external field the material is subjected to a series of flux jumps, and that the cumulative effect of these will introduce a slight dependence on the rate of increase of the field(7). On the other hand, it is a one-dimensional calculation and neglects the local character of flux jumps, thus yielding a rather pessimistic result.

The criterion is useful, however, in that it emphasises the important features of the instability. It shows, for example, that the field which may be screened is independent of the critical current density of the superconductor, since the higher the current density, the smaller the depth to which flux may penetrate before instability occurs.

It also shows that the field which can be screened is determined by the thermal capacity, $s\rho$, of the material. This explains the importance of porosity in sintered materials, since the thermal capacity of liquid helium is more than one hundred times greater than that of the sintered material, and therefore absorption of liquid helium by the porous structure will greatly increase its effective thermal capacity. A ring of average density 5.7 gm/cm^3 may absorb 0.04 gm/cm^3 of liquid helium, increasing its effective thermal capacity by a factor 20, and hence the field which may be screened by more than a factor 4.

Although a highly porous structure is desirable, it should be pointed out that high porosity resulting from large pore size is not very effective in aiding stability. Consideration of the thermal time constant of liquid helium shows that during the time of the flux jump, which is about 10^{-3} sec, heat can only be absorbed by the helium to a depth of about 5×10^{-4} cm. Thus a pore structure of dimensions much greater than 10^{-3} cm is not fully effective. It is equally obvious that a connected pore structure is necessary to allow the liquid helium to be absorbed, and that material such as that sintered in a bath of liquid tin, cannot screen high fields because the pore structure is blocked with excess tin.

EXPERIMENTAL EVIDENCE FOR THE STABILITY CRITERION

The criterion developed above makes two predictions which may be put to the test. First, that absorption of liquid helium into the porous structure increases the field which may be screened, and secondly, that the field which is screened is not a function of the critical current density of the material.

The screening field has been measured with several cylinders impregnated with wax to prevent the absorption of liquid helium. In order to observe

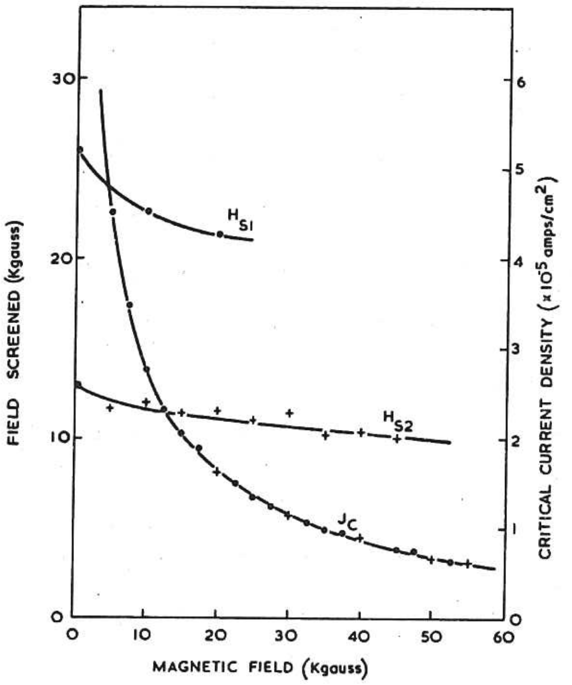

Fig. 4 (CLM-R 43)
Screened field for a cylinder before (H_{S1}) and after (H_{S2}) impregnation with wax. The critical current density before (dots) and after (crosses) impregnation is also shown

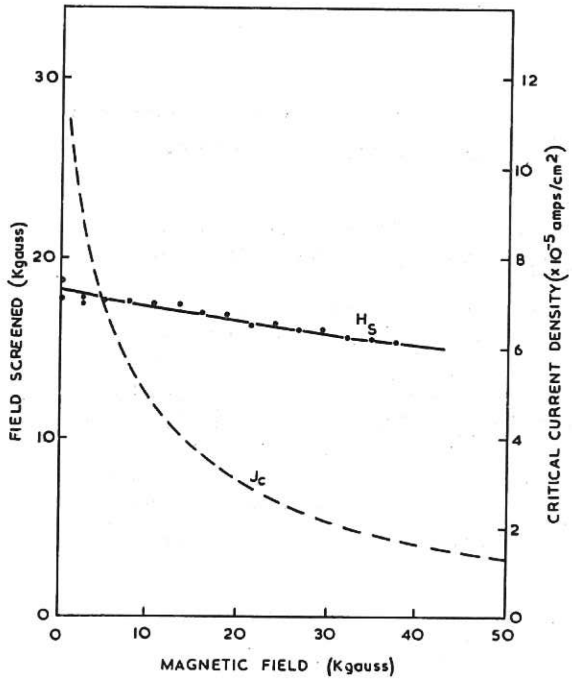

Fig. 5 (CLM-R 43)
Screened field and critical current density for a wax impregnated cylinder of sintered Nb_3Sn made from Niobium powder 1(a) sieved to less than -300 mesh

how the field which could be screened varied with the current density without changing any of the other parameters, measurements were made over a range of magnetic fields. Quenching the cylinder with a heater winding in the presence of a field before measuring the screening field effectively changes the current density. Results for a cylinder made from unsieved niobium powder 1 (a) are shown in Fig.4. and it is seen that impregnation with wax reduced the field screened by a factor 2 but did not affect the current density. Furthermore the screened field only changed 25% when the current density changed by almost an order of magnitude.

The measurements were repeated on a cylinder made from niobium powder 1 (a) sieved to - 300 mesh. This cylinder screened more than 55 kG before impregnation (i.e. had not quenched at the maximum field available) and screened 17 kG when impregnated with wax. The results are shown in Fig.5, and again the field screened is seen to change only slightly with current density. It is also seen that with the finer powders the ratio of the fields screened before and after impregnation is about 4 : 1 as expected.

5. CONCLUSIONS

The object of the work described above was to show that sintered Nb_3Sn could be a stable material for the construction of coils. It has been shown that average current densities comparable to commercially available wires and tapes are possible, and that suitably prepared material is stable in the presence of magnetic field changes up to at least 55 kG. Furthermore, the importance of the structure of the sintered material is now understood. It must also be emphasised that the results reported here have not been fully optimised either for current density or screened field and further improvements may well be possible.

It now remains to show that suitable methods of constructing coils from sintered material can be developed, and that the problems of supplying sufficient current can be overcome.

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