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A. Echarri and M. Spadoni : SUPERCONDUCTING Nb_3Sn: A review

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The methods of fabricating and increasing the critical current carrying capacity of superconducting Nb_3Sn are reviewed. The review covers metallurgical doping of the compound and irradiation effects by different types of bombarding particles. Mechanical problems presented in the winding of Nb_3Sn magnets, future problems to be tackled for low frequency pulsed superconducting magnets applications, and work in superconducting lenses for electron microscopy are included.

Superconducting Nb_3Sn: A review

A. Echarri and M. Spadoni

The phenomenon of superconductivity was discovered by Kammerlingh Onnes in 1911 [1] and in 1930 de Haas and Voodg [2] found that the superconducting state could not be destroyed for an alloy of lead–bismuth unless a magnetic field of over 2 T was applied. In 1933 Mendelssohn [3] reported results with a cylindrical solenoid made of a lead–bismuth alloy, but the maximum current density allowed to flow in the superconducting state was found to be quite low.

For more than twenty years afterwards the use of superconductors for the construction of magnets seemed to fade out. Probably, one of the reasons for this was also connected with the difficulties and expenses of liquid helium technology in this period.

In 1954, Hardy and Hulm [4] in a systematic study of compounds with the crystallographic structure A–15 found that V_3Si had a temperature of transition T_c = 17·1 K, that is, in the domain of liquid hydrogen, a much less expensive cryogenic liquid.

Subsequent research lead to the discovery by Matthias et al [5] of a T_c = 18·05 K for the A–15 compound Nb_3Sn.

It was only in 1961 that Kunzler et al [6] reported that Nb_3Sn remained superconducting at 4·2 K under high magnetic field (88 kOe) and high current density (10^4 A cm^{-2}).

Many works have been published since this date on A–15 type superconducting compounds and further progress has been made on increasing the temperature of transition and the upper limit of the magnetic field beyond which superconductivity is destroyed. In particular [7] for annealed Nb_3Al it has been found T_c = 18·4 K, and for Nb_3Ge that T_c can change between 6 K and 17 K depending on the cooling rate of the melt.[8]

The Nb_3Al–Nb_3Ge system reaches a T_c up to 20·7 K,[9–11] V_3Ga has T_c of up to 16·5 K,[12] and V_3Si up to 17·1 K.[4] Preparation in quartz crucibles can lead to erroneous statements about the high transition temperatures of some A–15 V_3X compounds, owing to the formation of $V_3(X_n\ Si_{1-n})$.[13]

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Unfortunately the technology of these compounds is not as developed as for Nb_3Sn, the only commercialized superconductor of this group. Perhaps the material most promising in the near future, belonging to this group, is V_3Ga, which has been prepared into wire form,[14] and is at present being industrially developed.[91]

Commercial superconductors

Towards 1961 the first superconducting alloys Nb–33% at Zr or Nb–25%Zr, with the possibility of constructing small solenoids with field strengths up to 50–60 kOe, were commercialized.

In 1965 several NbTi alloys were developed. Intimate metallurgical bonding with high thermal conductivity copper sheet improves the behaviour of the windings, allowing dissipationless currents on the solenoid not far from those measured on short samples. Magnetic fields of 80 kOe at 4·2 K in a 12 mm bore are not uncommon and have been reported in recent scientific literature.

Metallurgical work on superconducting VTi alloys and in Ti-rich Nb alloys is being done in order to use the minimum amount of expensive materials (Nb, V) while maintaining good superconducting properties. Something of this type has already been done in Russia [15] with Nb–75% Zr with very good results.

For a certain field intensity, the over-all current density in the solenoid and the price to be paid per ampere-metre can be seen in Figures 1 and 2 (from reference 16). It is obvious that up to 100 kOe NbTi is more convenient than Nb_3Sn from an economical point of view. Cost considerations however must be weighed against other factors involved in any experiment before a decision is made on the particular type of conductor.

Some d c applications of Nb_3Sn

For very high field strengths and higher field volumes it is normal practice to use NbTi on the external part of a magnet, where the amount of wire is high while the local

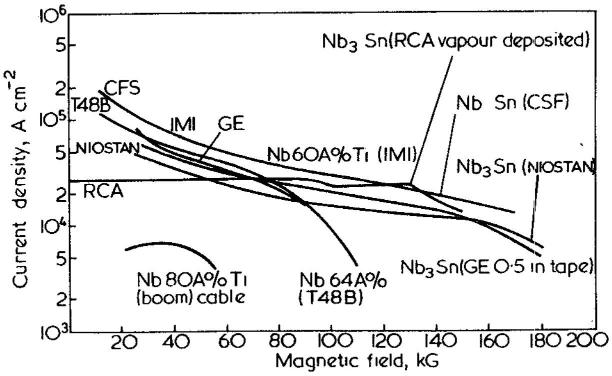

Figure 1. Over-all current density in solenoid windings for different superconducting materials, from reference 16

field is not great. The internal sections are then made in Nb_3Sn.

An example can be found on the 88 kOe half a metre bore magnet made by Lucas et al.[17] Another example is the 4·8 cm bore 250 kOe McGill University hybrid magnet. This magnet consists of a 41 cm bore 75 kOe NbTi magnet, inside which a 18·5 cm bore, 150 kOe Nb_3Sn magnet is located; the final field is reached with a cryogenically cooled 4·8 cm bore aluminum insert.[18] For large scale experiments on plasma research at the NASA Lewis Research Centre a 3·30 m long superconducting magnet is used. It consists of four coils 25 cm i d, 10 cm length, wound with Nb_3Sn vapour deposited RCA ribbon, four coils 25 cm i d, 30 cm length; the internal windings being made with GE Nb_3Sn stainless steel reinforced copper clad conductors and the outer windings from square section copper-clad NbTi composite. These eight coils are each spaced 15 cm apart, producing a central field of 72 kOe.

At the ends of these eight coils there are two 15 cm i d, 25 cm o d, 30 cm length 'mirror' coils wound with 0·23 cm wide RCA ribbon and producing a central field of about 137 kOe.[19]

On the other hand smaller type of coils can be wound with different tapes of Nb_3Sn, which have decreasing prices related to decreasing current capacity at a given field. Such an example is the 5·5 cm bore 100 kOe, 6 mm window Frascati split coil, producing an 80 kOe central field for a 4 cm window aperture.[20]

For a given field of the magnetic lens in an electron microscope, spherical aberrations, which limit the resolving power, increase with increasing accelerating voltage. This is a drawback, since increasing accelerating voltage is a way of achieving higher resolution. To decrease spherical and chromatic aberrations, higher magnetic fields for a given accelerating voltage have to be used. The axial magnetic field gradient must also be as high a possible for a given field because aberrations are lower when the field gradient increases. High fields and current stability can be obtained with superconductors, consequently the use of superconducting properties in electron microscopy may be of interest.[21] There are in fact good reasons to use superconducting lenses for accelerating voltages higher than 400 kV.[22] Field gradients from 90 to 140 kOe cm^{-1} have been achieved by trapping flux in Nb_3Sn sintered discs.[23,24] Cylindrical short solenoids made with superconducting ribbon have the disadvantage of introducing astigmatism due to distortion produced by the current leads; the problem is overcome by using the shielding properties of Nb_3Sn hollow cylinders.[24] To obtain first order focusing superconducting quadrupoles have been suggested by A. V. Crewe.[19]

Since a discussion of all the possible applications of high field superconductors is not within the scope of this paper, we will only mention a proposal [25] for a Nb_3Sn d c power transmission line to carry 10^5 megawatts over a distance of 1 000 km.

Progress towards a c applications of Nb_3Sn

Shielding currents are induced in a superconductor to oppose any change in applied field. Experimentally it is observed that such currents are unstable around the field for which the current sheet extends to the centre of the conductor; the decay of the currents release the stored energy as heat.

Because the thermal conductivity of a superconducting alloy is sometimes a thousand times lower than that of a pure metal, magnetic flux moves much more rapidly than heat.

Thus for a wire of diameter $2a \sim 0{\cdot}02$ cm having a current density $J_c, \sim 3 \times 10^5$ A cm^{-2}, the magnetic energy, if suddenly released is enough to increase the temperature of the material to about 10 K. However if the same material is subdivided into filaments about 0·002 cm, the temperature rise would be only about 0·3 K per filament.[26] Moreover if such filaments are in intimate metallurgical bonding with a high thermal conductivity–high electrical conductivity material, then in the case of a local transition to the normal state of the superconductor, such material acts both as an electrical and thermal shunt.

Multifilamentary wires of superconducting materials imbebbed in a copper matrix were proposed by Chester.[27] This configuration reduces the losses when operating in a c or pulsed currents, and also improves the d c behaviour at low fields, where sudden returns to the normal state (flux

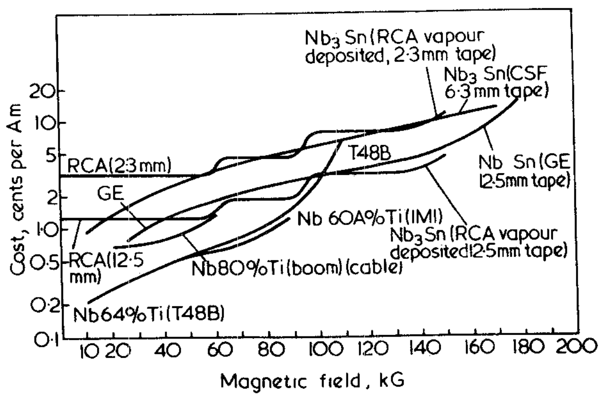

Figure 2. Cost per A m, from reference 16

jumps) are more likely when charging a superconducting magnet. An extensive experimental and theoretical work can be found in reference 26.

Multifilament NbTi wires are commercially available, but for Nb_3Sn progress has been hampered by its extreme brittleness. Nb_3Sn wires of diameter of 0·043 cm, consisting of up to 73 Nb_3Sn filaments of 10^{-3} cm diameter (10 μ or 10 μm), have been developed by Kaufmann and Pickett.[28]

A very extensive review on a c losses in superconductors has been given by S. L. Wipf.[29] As a general rule it is found that losses per cycle are independent of the frequency up to at least 20 kHz. He gives the following universal formula for Nb alloys

$$\text{loss per cycle per cm}^2 = 4{\cdot}22 \times 10^{-9} \frac{(H-\Delta H)^3}{J_c} \qquad \ldots(1)$$

with the dimensions of the numerical constant J A Oe^{-3} cm^{-4}. In (1) H is the applied field and ΔH is a material dependent parameter which rarely exceeds 1 kOe; this being many times the order of the lower critical field H_{c_1}. It seems doubtful, according to the above formula that a c cables made with superconducting Nb alloys rather than pure Nb can be of interest for appreciable line lengths, the lower critical field H_{c_1} of a Nb alloy being generally lower than H_{c_1} of pure Nb.

However for other applications such as superconducting pulsed magnets for proton-synchrotrons it is estimated that if losses at 4·2 K are as high as 20 W m^{-1}, the refrigeration cost can be offset by the increased power and/or savings over a conventional synchrotron. The dissipation in a typical 60 kOe, 10 cm aperture diameter synchrotron magnet wound with 0·025 diameter NbTi wire is about 500 W m^{-1} per magnet length when a 3 s cycle time is envisaged. In order to reduce the losses by a factor 25 to 50 multifilamentary composites of average strand diameter 5 to 10 μm are necessary.[26] For the simple case of a composite of length $2l$ cm, consisting of two sheets of superconductor, each of thickness d cm, separated by w cm of normal metal of resistivity ρ (Ω cm) and immersed in a magnetic field perpendicular to l and w, which is increasing at a uniform rate $\dot{H}$, Oe s^{-1}(1Oe = 80 A m^{-1}), there is a critical length l_c given by

$$l_c^2 = \frac{2 \times 10^8 \rho \lambda_1 J_c d}{\dot{H}} \frac{w}{w+d} \qquad \ldots(2)$$

λ_1 is an appropriate space factor for a superconductor in the form of separate filaments. It can be shown that if $l < l_c$ only a fraction l^2/l_c^2 of the current will cross the normal matrix. For a long length of conductor this is achieved by twisting the conductor about its axis with a pitch very much less than l_c. For a typical value of $\dot{H} \sim$ 50–60 kOe s^{-1} the required twist pitch is far too small to be feasible using only a copper matrix. Equation 2 indicates that higher resistivity material is desirable. NbTi copper–nickel alloy – Cu twisted multifilamentary wires, having up to 1 045 NbTi 10 μm diameter filaments in a 0·04 cm diameter composite wire, have therefore been industrially developed[30,31] to reach a better compromise between minimum a c losses and maximum allowable

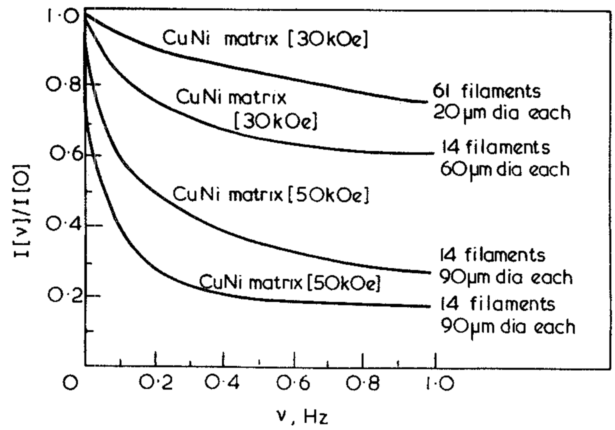

Figure 3. Effect of strand diameter on the improvement of a c transport currents for small coils, wound with twisted multifilamentary NbTi, from reference 26; a c tests for multifilamentary 10 μm strand diameter Nb_3Sn composite are not yet available (1 Oe = 80 A m^{-1})

currents which approaches the performances of the same material when used in d c applications. Figure 3 shows the improved performances with decreasing strand diameter which have been achieved so far with NbTi pulsed magnets.

Twisted multifilamentary Nb_3Sn composites are not yet commercially available. However according to equation 2 the higher critical currents achieved by Kaufmann's and Pickett's multifilamentary wires over the best NbTi suggests that perhaps copper–nickel alloy sheathing would not be necessary to obtain the required pitch for pulsed synchrotron applications.

The NbSn phase diagram

The knowledge of the phase-diagram of the system NbSn is very important, the composition, temperature regions of the different possible intermetallic compounds give useful information about the techniques to be followed in any industrial process.

In about seven years, several papers[32–42] have been published on this argument. Now it is generally accepted[42–44] that in the niobium–tin system there are three intermetallic compounds with structures corresponding to the formulae Nb_3Sn, Nb_6Sn_5, and $NbSn_2$.

Figure 4 shows what is in our opinion the more likely phase diagram, which is the result of Vieland's high temperature measurements up to about 1 300 C[45] and of measurements taken from reference 42, and it is in agreement with more recent experimental work.[46] From the phase diagram it can be seen that by melting Nb and Sn with more than 30% Sn in weight, only the intermetallic compound Nb_3Sn plus quite pure Sn is obtained as the temperature is lowered down to 930 ± 15 C.

Below 930 C Nb_6Sn_5 with T_c = 2·07 ± 0·25 K and $NbSn_2$ with T_c = 2·68 ± 0·03 K[47] can exist. Regardless of the preparation method it is very important to heat up to the desired temperature and afterwards to cool down quickly in order to avoid the formation of the low T_c

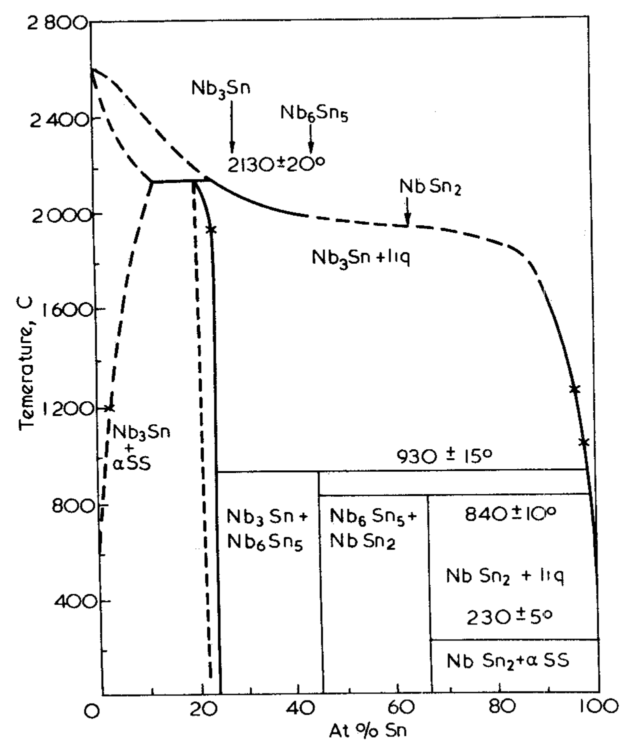

Figure 4. Probable phase diagram for NbSn system according to references 42, 45, and 46

phases,[48] which can deteriorate the behaviour of the material.

Nevertheless it could be possible that a careful control of the presence of the other two phases in the Nb_3Sn results, by the introduction of pinning centres, in a rise of the critical current; some supporting evidence can be drawn from the experimental work of reference 49.

Fabrication of Nb_3Sn tapes by hydrogen reduction of gaseous chlorides

This method was developed by Hanak [50] at RCA Laboratories. The apparatus consists of a deposition chamber and two chlorinators in which metallic Nb and Sn react with Cl_2 to form $NbCl_4$ and $SnCl_2$. The two chlorinators and the quartz deposition chamber are fitted with separate furnaces. In the reaction chamber the mixed gaseous chlorides flowing in from the chlorinators react with H_2 which diffuses counter stream to the mixture. The moving substrate is heated to about 1 000 C in the reaction chamber with slotted carbon electrodes. The rest of the reaction chamber is kept at a temperature low enough (~ 700 C) to maintain the incoming metal chlorides in the gaseous state. A chemical reaction takes place in which solid Nb_3Sn and solid $NbCl_3$ are formed. Clogging of the walls by solid $NbCl_3$ can be partially overcome by adding a controlled amount of HCl.[51] In this way up to 1 000 m length could be made in a single run. A different experimental set-up for depositing Nb_3Sn from the gas phase without clogging by $NbCl_3$ was described by Arkharov et al. [52] Here solid $NbCl_5$ is heated to 120–180 C and hydrogen passes through a reservoir at 0 C saturated with stannic chloride vapour. All the reaction is then at a temperature much too low to form $NbCl_3$ in appreciable quantities, with the exception of narrow regions around the substrate which is heated to 1 000–1 200 C.

Another means of minimizing clogging is to allow into the reaction chamber enough $NbCl_5$ to react with the $NbCl_3$ formed to obtain reconversion to $NbCl_4$. The temperature of the walls in this case is about 730 C.[53]

The flexible substrate used by RCA is in Hastelloy, a nickel-base alloy made by Stellite Division, Union Carbide Corp, Kokomo, Indiana. Hastelloy has a thermal expansion coefficient greater than that of Nb_3Sn, inducing therefore a compressive stress within the Nb_3Sn in cooling down to lower temperatures. The relationship between external tensile forces and the thermally induced compressive stresses is discussed in more detail at the end of this article.

The kinetic of growth of Nb_3Sn layers obtained by diffusion of Sn in Nb

Niobium ribbon or wire has mechanical properties equivalent to a good steel. It is possible to obtain Nb_3Sn layers from a Nb substrate by diffusion at high temperatures of Sn in Nb. Kunzler, in his pioneering paper, used a diffusion technique, known as cladding, to obtain superconducting Nb_3Sn wires.[6] These wires were formed by reacting at 1 000 C a stoichiometric mixture of powders of Nb and Sn contained in a Nb tube.

Vapour diffusion is a modification of Power's method[54] used by De Sorbo.[55] In this method a Nb wire is heated in tin vapour, the whole assembly being previously evacuated to a pressure of about 10^{-8} mmHg ($\sim 10^{-6}$ N m^{-2}). Electrophoretic keying of Sn particles in Nb wires or ribbons followed by convenient heat treatments is a method patented by IMI (Kynoch) Ltd,[56] while electrophoretic deposition over a metallic substrate of Nb and Sn powder mixture is a propietary process of English Electric Co.[57]

Dipping is a direct immersion of Nb in molten Sn in a high vacuum or in inert atmosphere in order to avoid interstitial contamination of Nb.[58]

This method has proved very popular and is currently used by General Electric, Norton Corporation, Thomson–Houston, and others.

The phase diagram alone cannot furnish information on the mechanism and kinetic of growth of Nb_3Sn for a diffusion process. It is impossible to derive from it the influence of the temperature and of the reaction time on the thickness of the Nb_3Sn obtained. In the case of Nb_3Sn produced by dipping of Nb in liquid Sn (for greater details see references 58–60), assuming that the only process leading to the formation of the intermetallic component layer is a diffusion process, the thickness x should increase according to the law

$$x^2 = 2Dt \qquad \ldots(3)$$

where D is the diffusion coefficient and t the reaction time. The temperature dependence of D is

$$D = D_0\, e^{-E/RT} \qquad \ldots(4)$$

with E the so-called activation energy, R the gas constant, and T the absolute temperature.

The results of Smulkowski are in good agreement with (3) and (4), as they provide a parabolic dependence of the thickness of Nb_3Sn as a function of reaction time, indicating further that for a fixed time, the thickness increases as the temperature is raised. This is the normal case of a positive activation energy.

However more recent results obtained by Old et al,[48] seem to indicate a time dependence of the thickness in the form

$$x = C\,t^{0{\cdot}36} \qquad \ldots(5)$$

and from 950 C to 1150 C, the range of temperatures studied, the thickness of Nb_3Sn decreases with increasing temperature. The explanation for these results was that the Nb_3Sn forms partly by diffusion and partly by a solution-deposition mechanism. In order to account for the decrease in thickness with increasing temperature, they estimated that the apparent activation energy, given by the difference between the activation energies for diffusion and solution was $-9{\cdot}7$ Kcal g atom^{-1}

The kinetics of formation must in any case depend on the heating and cooling rates, the diffusion conditions (dynamic or static), and probably, as well the quantity of tin in the crucibles.

Metallurgical factors affecting the critical current density

A feature of superconducting materials able to carry high currents without dissipation is that, under the action of a magnetic field they present a co-existence of normal and superconducting regions, generally described as the 'mixed state'. For fields below a certain value H_{c_1}, known as lower critical field, the magnetic energy is not high enough to allow a penetration of the magnetic field inside the sample; therefore the magnetic induction B is zero. For fields above H_{c_1} it is energetically favourable for the sample, and allows the penetration of the field in cylindrical regions, which are non-superconducting. Each of these regions carries one quantum of flux $\phi_0 = 2 \times 10^{-7}$ G cm^{-2}.

Increases in the field are counterbalanced by the superconductor by allowing normal cylinders called flux lines to be created inside, each having a radius ξ, known as the 'coherence length'. This goes on until, at a certain field H_{c_2} the material collapses in bulk to the normal state. The coherence length ξ at a temperature $T < T_c$ is related with H_{c_2} by

$$\xi(T) = \left[\frac{\phi_0}{2\pi}\,\frac{1}{H_{c_2}(T)}\right]^{1/2} = \frac{564}{H_{c_2}(T)^{1/2}} \qquad \ldots(6)$$

where $\xi(T)$ is already in Å if H, $H_{c_2}(T)$ is in kOe (1Oe = 80 Am^{-1}).

In the presence of a transport current density J in a superconducting sample, there is a Lorentz-type force

$$\vec{f}_L = \frac{\vec{J} \times \vec{\phi}_0}{c}$$

on each vortex line.[61] The vector $\vec{\phi}_0$ has the direction of the external applied field and its modulus has the value of the quantum of flux. If the number of flux lines per unit surface is n then the induction is $\vec{B} = n\vec{\phi}_0$; the resulting force per unit volume is then

$$\vec{F}_L = \frac{\vec{J} \times \vec{B}}{c} \qquad \ldots(7)$$

Flux lines move in response to this force unless suitable pinning centres impede this movement. The higher the pinning forces are, the higher the Lorentz forces have to be to unpin the flux lines. Therefore, for a certain applied field, the higher the pinning force, the higher will be the maximum current density J_c which can flow without dissipation. J_c results from the balance between pinning forces and Lorentz forces.

If J_c is in A cm^{-2} and B in G, the net pinning force per unit volume F_p in dyne cm^{-3} (1 dyne = 10^{-5} N) is given approximately by $F_p = BJ_c/10$. By magnetization and critical currents measurements on a sample it is possible to find at which field H the pinning force is a maximum.

From a theoretical point of view, according to Friedel et al,[62] optimum pinning can be achieved for a distance between flux lines of the same order as the size of the pinning entities. For flux lines arranged in a triangular lattice at moderate induction

$$B = \frac{2\phi_0}{d^2\sqrt{3}} \qquad \ldots(8)$$

where d is the lattice spacing.

Typical values for ξ range from 400 Å if H_{c_2} = 2 kOe to 40 Å if $H_{c_2} \sim$ 200 kOe as in the case of Nb_3Sn. Thus if maximum pinning is wanted for a field of about 150 kOe ($B/H_{c_2} \sim 0{\cdot}75$) the size of the pinning entities should be of the order of 120 Å. Calculations of interactions between flux lines and some kind of defects have been made by Friedel[62] for the case of voids, by Toth and Pratt[63] for the case of coherent precipitates, by Webb[64] and Kramer and Bauer[65] for screw and edge dislocations. Labusch[66] has given very general equations which include some of the preceding cases.

It is clear that clustering of punctual defects, as produced by irradiation[67] or dislocations rearrangement[68] into cell walls for example, will be more effective than single defects or a uniform distribution of dislocations.

Increase of critical current by doping

Appropriate doping of Nb_3Sn can increase its current density. Thus, De Sorbo[55] showed that by adding zirconium of about 10–20 at % to the original Nb wire, increases in critical current of 3–4 times the original values were obtained.

The influence of different concentrations of Zr for Nb_3Sn obtained by cladding, dipping, or vapour diffusion has been extensively studied by Saur et al.[69]

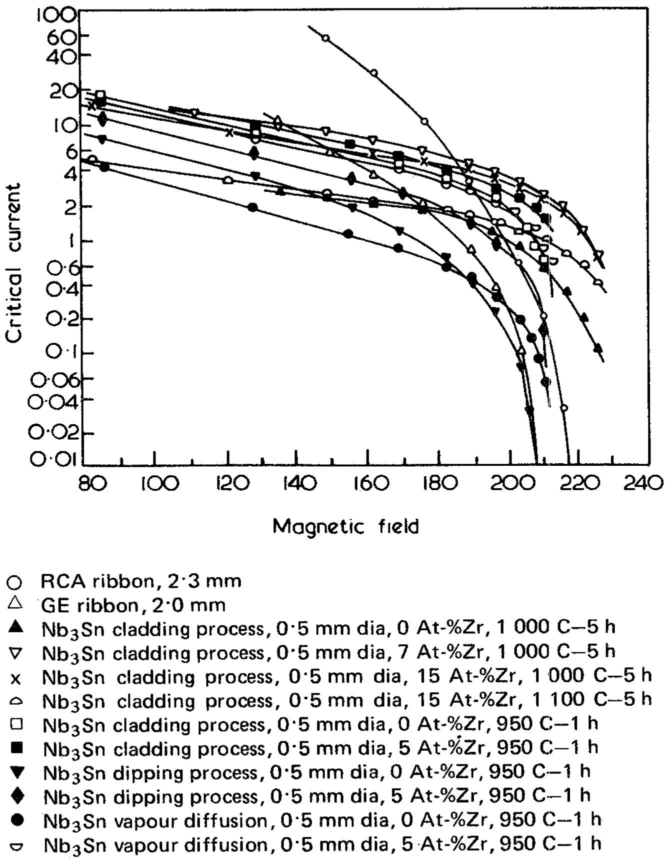

Figure 5. Critical current curves of Nb_3Sn diffusion layers with different preparation conditions in transverse magnetic field, from reference 69

It is found that the doping with Zr up to about 12 at % that is, in the limit of solid solution for the Nb rich side of the NbZr phase diagram,[70] increases the critical current independently of the method used.[55,69] Figure 5 shows Saur's results[69] for Nb_3Sn diffusion layers with different preparation conditions in transverse magnetic field. Although the geometrical dimensions of Saur's wires differ from those commercial wires, it seems quite likely, judging by earlier performances of such commercial wires, that both RCA and GE wires have been doped as well.[71–73]

De Sorbo's result for Zr contents higher than 15% seems to indicate a spurious effect on the current carrying capacity due to the presence of two phases in the eutectoid region of the NbZr system. Further work would be advisable in order to clarify this point.

By doping with ZrO_2 particles, Benz,[74] obtained a critical current density higher than for undoped specimens, which does not decrease as the Nb_3Sn layer is increased in contrast to the results of many other workers. He also observed that for a transverse applied field the current density was constant regardless of the angle between the transverse field vector and the wide side of the tape which is also in contrast to preceding results. Figure 6 shows Benz's results compared with the results of reference 75, which are typical of many other authors. Most probably preceding observations could be accounted for by the existence of Nb_3Sn layers consisting of single phase columnar grains while in ZrO_2 doped samples heterogenities increase with thickness and the material is less orientation sensitive.

Benz's results seem particularly important because if the current density is lower when the field vector is no longer parallel to the wide side of the tape, then transitions to the normal state can easily occur in the regions around the external edges of a magnet.

Benz plotted the volume pinning strength J_cB versus B/H_{c_2} finding a maximum J_cB when $B/H_{c_2} \sim 0{\cdot}3$, that is $H_{appl} \sim 70$ kOe.

The distance d between vortex lines at this field is roughly $d \sim 200$–240 Å, while the size of ZrO_2 particles was 200–1 000 Å. It is not known what percentage of particles had sizes between 200–250 Å, but if the above remarks concerning pinning strength apply here, then a fairly high percentage should have been within this range of sizes.

It is curious too that Hanak and Enstrom[76] find the maximum BJ when $B/H_{c_2} \sim 0{\cdot}3$ ($H_{appl} \sim 70$ kOe). The dimensions of the grain boundaries, responsible for pinning in their alloys according to them, were of the order of 385 Å. Moreover Hart et al[77] studied the current carrying capacity at 46 kOe for oxygen doped Nb_3Sn samples, having precipitates spaced 200 Å and with average size 50 Å, and they inferred that the pinning force at 70 kOe should be of the same order of magnitude as derived in references 74 and 76.

It could be that Hart's precipitation method (see also references 72 and 73) gives an optimum pinning strength towards higher B/H_{c_2} values than with other methods; no high field measurements however have been reported to date by these authors.

Irradiation effects on Nb_3Sn

Another method of increasing the critical current density is to produce clusters of point defects such as Frenkel pairs,

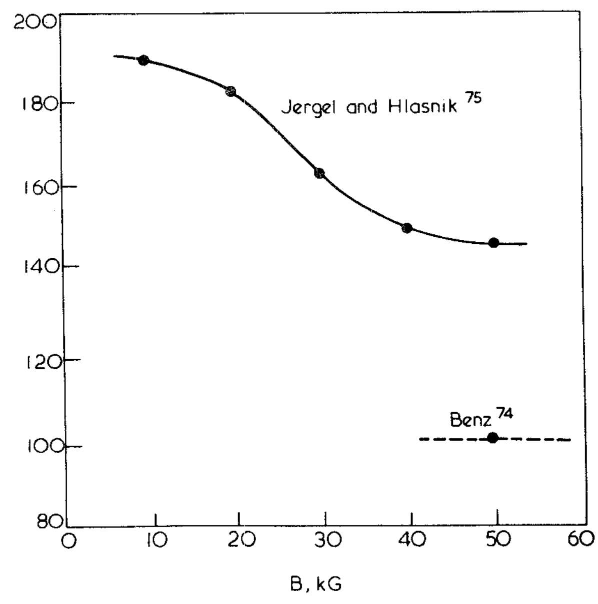

Figure 6. Dependence of anisotropy on magnetic field, from references 74 and 75

which can be obtained by irradiation. There is not as yet a practical application of irradiation to superconductivity. Irradiation is used today for very rapid polymerization of paints and plastics in the motor car and cable sheathing industries. Many experiments have been undertaken to gain knowledge of how a superconducting magnet will behave after a long period, in a radioactive environment.

The passage of particles through solid materials produces defect clusters, the possibility of the mean number of displaced atoms ν constituting a cluster depending upon the radiation dose, the energy of irradiating particles E_x, and the previous cold-work history of the material.

By varying the bombarding particles from electrons to protons to deuterons to alpha particles, the probability of having larger clusters (assuming the same incident energy and the same integrated flux) increases, due to an increase of the mass of the incident particles.[67]

Moreover in the case of a metal doped with fissionable impurities such as U_{235}, the total kinetic energy of fission fragments being about 162 MeV [78] and the mass of the fragments being appreciably great, considerably more damage is obtained. Experiments with high field superconductors such as Nb_3Al and V_3Si doped with uranium and post-irradiated have been reported by Bean et al.[79]

The concentration ratio of clusters $\rho(\nu)$ (cm^{-3}) of the clusters for neutrons and protons was found in reference 67 to depend on the ratio N_p/N_n with $N_{n,p}$ number of incident particles per cm^2. Assuming that all clusters with ν or more single defects were equally effective pinners, he deduced the ratio N_p/N_n necessary to give the same critical current I_c enhancement (measured at the same field) in his proton irradiation experiment at 2·83 MeV in Nb_3Sn as the enhancement found by Cullen et al [80–83] with neutrons of 1·5 MeV. He obtained $N_p/N_n = (3–6) \times 10^{-2}$, that is, $N_p \sim (1–2) \times 10^{16}$.

This means that considerable less proton flux is necessary to achieve the same increase in critical current.

Obviously enough, depending on the pre-irradiated cold-work state of the material, on the energy E_x, and the integrated flux, 'optimal' clustering leading to increased critical current values, or clusters coagulation, leading eventually to a decrease of the critical current, can be obtained.

Thus, in the experiment reported in reference 67 such a coagulation process appears to happen to an integrated flux bigger than $8–9 \times 10^{16}$ protons cm^{-2}. It appears also that the maximum I_c enhancement in this experiment is about 2·5 times the pre-irradiated value.

Care must be taken however on handling these comparisons; a rough estimate indicates that for Cullen's Nb_3Sn samples the pre-irradiated critical current density J_c (as opposed to critical current) is higher than that in reference 67. No experimental results have been reported as yet on samples with the same pre-irradiated metallurgical history as a function of integrated flux energy, type of particles, and identical geometry.

As an example of the above remarks, experiments done on Nb_3Sn [84] with 15 MeV deuteron irradiation at doses up to 10^{17} d cm^{-2}, showed an increase or a decrease in J_c depending upon the previous cold-work state of the material. The decrease of J_c in samples that had previously the higher current carrying capacity could be accounted for by a final size of the clusters much larger than the distance between flux lines in that range of fields and hence less effective as a pinning site.[62]

For deuterons with $E_x = 3$ MeV it was found that the critical current at 50 kOe was enhanced somewhat more than with protons of the same energy and total integrated flux (or lower energies),[85] as would be expected from the fact that the deuteron mass is greater than that of the proton.

Further evidence of the role played by the initial state of the material and the final size of the radiation produced pinning centres can be sought by studying the effects produced by neutron doses up to 2×10^{19} N cm^{-2} (with $E_x \sim 1$ MeV) on single crystals of zone refined niobium,[86] for which measurements up to H_{c_2} have been made.

There (see Figures 1, 2, 4, 6 of reference 86), it can be seen that not only irreversibility, H_{c_2}, and remanent moment increase with increasing neutron doses, but also a minor peak in the magnetization curve near H_{c_2} appears. For these experiments applying equation 6 we have ξ (4·2 K) ~344 Å for Nb–B and ξ (4·2 K) ~326 Å for Nb–A, and it is probable that the size of the clusters produced under such heavy irradiation dose, is of the order of 400 Å, that is, the pinning has been enhanced just before H_{c2} and this gives the peak effect.

Mechanical problems presented in the winding of Nb_3Sn magnets

In order to avoid a long winding of superconducting solenoid returning to the resistive state at a transport current lower than the critical current which a short length of the wire was able to carry, intimate metallurgical bonding with a high thermal conductivity metal is made. This however reduces the average current density of the conductors.

In other words the packing factor λ = conductor cross-section/total cross-section, decreases with the additional amounts of normal metals. This kind of superconducting material is known as a composite superconductor. A very extensive discussion of the optimal ratio of normal conductor to superconductor in each particular problem can be found in Montgomery's book.[87]

For magnets in which electromagnetic forces are important, Nb_3Sn tapes are made as a multi-component composite with a high strength material such as stainless steel, a low resistivity normal material, and the superconductor. An example is the General Electric tapes [88] shown in Figures 7a and b. Figure 7a is a schematic view of a symmetric Nb–Nb_3Sn–eutectic PbSn–copper–stainless steel composite conductor. Figure 7b shows a non-symmetric composite having copper as one of the outer layers, for better joints in subsequent useage. Figure 7c shows the type of ribbon usual when co-deposition from the gas phase by the RCA technique is used.

Copper and stainless steel have nearly similar thermal expansion behaviour when cooled, the thermal expansion of

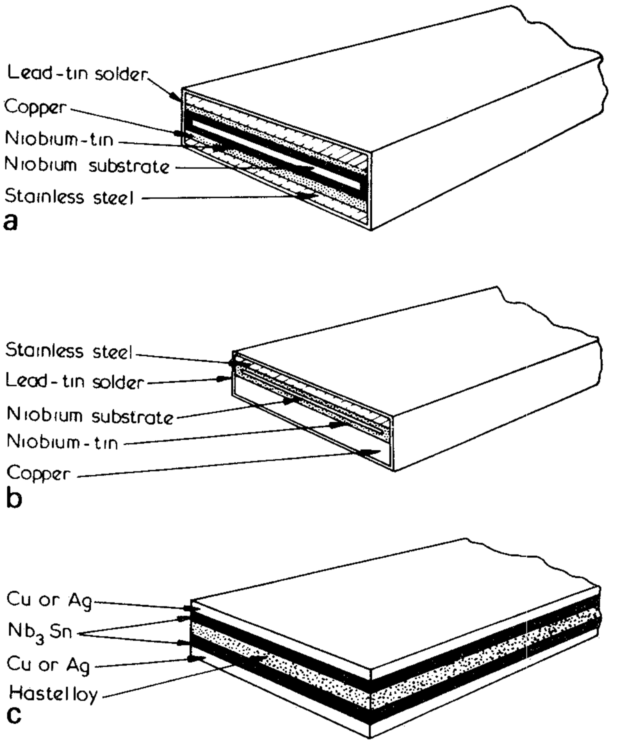

Figure 7. a and b Schematic view of symmetric and non-symmetric General Electric composite conductors; c coated RCA ribbon with Hastelloy substrate

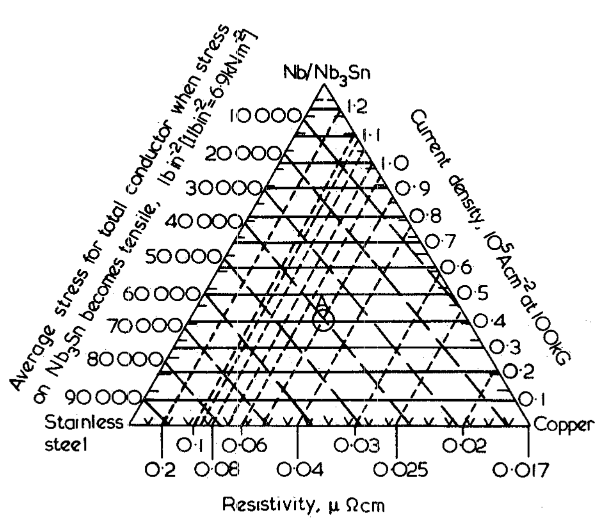

Figure 8. Current density, resistivity and average stress for a laminated conductor when the stress on the Nb/Nb3Sn becomes tensile. Solid lines: current density. Short dashed lines: resistivity. Long dashed lines: design stress level (see text); from reference 88 (1 kg mm^{-2} ~ 1 422 lb in^{-2})

both being larger than Nb_3Sn. This leads to a very large compressive stress on the Nb_3Sn layer on cooling.[51,88] If an external tensile force is applied to the over-all composite then the compressive stresses are reduced on the Nb_3Sn. When the external tensile force reaches a certain level the stress on the Nb_3Sn switches from compression to tension. Such a limit stress was taken by reference 88 as the design stress of a composite. He found that this was a safe limit to prevent both fracture of the Nb_3Sn and cyclic plastic strain of the low resistivity normal material which increases its resistance.

Nb_3Sn and the other technologically important superconductors have a low thermal conductivity in the superconducting state and a high electrical resistivity in the normal state. Thus a low resistivity normal metal coating is very important, acting both as an electrical and thermal shunt in the case of a local transition to the normal state in an energized coil wounded with a Nb_3Sn tape.

Bends around a radius less than 250 times the thickness of the Nb–Nb_3Sn layer can start fracture of the outer layers (on the tension side) of the Nb_3Sn.

Since electromagnetic forces on the windings of a magnet depend on the distance to the centre, current density, and magnetic field, very large forces are expected in the case of very large high field superconducting magnets. A full discussion of this problem with appropriate bibliographical references has been made in reference 89. Such calculations were used by Appleton[90] for the calculation of electromagnetic forces of a 2·22 m i d, 2·58 m o d, 0·55 m long NbTi magnet used for the superconducting stator of the 8 000 h p (1 h p = 0·75 kW) d c motor.

Benz's diagram for the GE reinforced tapes of Nb_3Sn is shown in Figure 8. The solid lines are constant current density lines, the short dashed lines represent constant resistivity, and the long dashed lines represent the design stress. Thus a composite conductor, represented by point A in the diagram, will have the following characteristics: design stress = 4 x 10^4 lb in^{-2} (280 MN m^{-2}), current density = 4 x 10^4 A cm^{-2} at H = 100 kOe (8 x 10^6 A m^{-1}), and normal state resistivity = 0·05 x 10^{-6} Ω.

Nb_3Sn versus NbTi: present market trends

An effort has been made to bring up-to-date the information in Figure 2. The task however proved to be very difficult in the case of constructed solenoids. Twelve companies (six American, two English, two German, one French and one Japanese) were asked to give details of prices and characteristics of their NbTi or Nb_3Sn conductors. Only six replied providing prices as well as the technical information requested, one company having decided to close down their superconducting products sales office. Calculated prices per ampere-metre were therefore made taking into account short sample characteristics. It is hoped that Table 1 will provide market trends and information about the best choice of conductors.

Since the higher the average current density in a composite conductor the less amount of material necessary to produce a certain field H, twisted multifilamentary conductors having a rather low normal matrix to superconductor ratio, high current density, and high stability are of interest for medium-sized magnets. Perhaps rectangular

Table I*. Comparison of the technical and economical characteristics of NbTi and Nb_3Sn conductors

	Material type	Price US cents x metre	I_C, A (50 kOe)	J_C, A cm^{-2} (50 kOe) (1 Oe = 80 A m^{-1})	Price† (50 kOe)	I_C, A (80 kOe)	Price† (80 kOe)	I_C, A (100 kOe)	Price† (100 kOe)	Notes
IMI NbTi 'Single core'	1/0·4/0·25	31·0	67	5·3 x 10^4	0·46	35	0·88			
	1/0·4/0·20	25·8	44	3·5 x 10^4	0·59	23	1·13			
VMCo NbTi 'Single core'	1/0·35/0·25	18·9	50	5·2 x 10^4	0·38					
	1/0·35/0·25	28·0	57	5·94 x 10^4	0·49					
NRC NbTi T 48 B 'Single core'	1/0·33/0·25	37·8	70	8·15 x 10^4	0·54	36	1·05	14	2·70	
	1/0·46/0·35	67·7	130	7·9 x 10^4	0·52	62	1·09	25	2·71	
	1/0·61/0·48	110·7	200	6·8 x 10^4	0·55	100	1·10	40	2·77	
IMI NbTi multifilamentary composites	FMA 61/0·5/0·042	60·0	125	6·33 x 10^4	0·48	60	1·00			Twisted 25 mm pitch
	FMA 61/0·4/0·034	43·1	82	6·5 x 10^4	0·52	38	1·13			
	FMA 61/0·33/0·023	36·9	57	6·7 x 10^4	0·65	28	1·32			
	TC 1045/0·4/0·008	147·7	76	6 x 10^4	1·94	35	4·22			Copper matrix, twisted
	CN 61/0·25/0·021	61·5	32	6·66 x 10^4	1·92	15	4·10			Copper nickel mat. twisted
Thomson Houston composite	THN 912-180 30/10 x 1·8/0·25	738·5	2000	1·1 x 10^4	0·37					
NRC NbTi multifilamentary composites	1160/3 x 3/0·05	800·0	1500	1·67 x 10^4	0·53					Twisted 80 mm pitch. The critical currents here reported are at 55 KOe
	1440/4 x 4/0·05	686·1	1500	0·94 x 10^4	0·46					
	1160/3·6 x 3·6/0·05	836·9	1500	1·15 x 10^4	0·56					
	21/2·9 x 1·5/0·27	400·0	1100	2·52 x 10^4	0·36					
	320/3·6 x 3·6/0·1	686·1	1500	1·15 x 10^4	0·46					
	820/2·6 x 2·6/0·05	400·0	1000	1·48 x 10^4	0·40					
GE Nb_3Sn composites	22CY009 Tape/5 x 0·1	330·7	320	6·7 x 10^4	1·03			120	2·75	
	22CY015 Tape/12·07 x 0·09	492·3	400	3·5 x 10^4	1·23			150	3·28	
	22CY030 Tape/12·7 x 0·1	840·0	810	6·2 x 10^4	1·04			300	2·8	
Plessey Nb_3Sn composites	914/1/00003 Tape/6·4 x 0·053	161·5	230	6·7 x 10^4	0·50			110	1·47	
	914/1/00080 Tape/6·48 x 0·109	290·7	450	6·35 x 10^4	0·65			210	1·38	
	914/1/00071 Tape/12·88 x 0·53	280·0	450	6·6 x 10^4	0·62			210	1·33	
	914/1/00073 Tape/12·88 x 0·109	556·9	900	6·42 x 10^4	0·62			420	1·32	

* 1/0·4/0·25 means 1 core of 0·25 mm dia. stabilized with copper to make wire of 0·4 mm total diameter; 30/10 x 1·8/0·25 means 30 filaments of 0·25 mm diameter each in a rectangular composite of section 10 x 1·8 mm

† US cents per A m

or square twisted conductors would also be interesting due to the higher packing factor on this geometry.

It is clear that with some reduction in manufacturing prices and/or higher current densities by appropriate doping (optimal current density at the required field) Nb_3Sn can easily be competitive with other conductors even at not very high field intensities.

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