NEW SUPERCONDUCTING MATERIALS FOR MAGNET APPLICATIONS*

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Abstract

The "state of the art" for niobium titanium composite conductors is reviewed. The properties of multifilamentary A15 conductors are described and compared with those of NbTi composites.

1. Introduction

Most of the superconducting materials referred to in this paper are not "new" in the usual sense; their superconducting parameters have been well known for some time. What is new about them is their possible development into modern conductors for use in magnet fabrication. For the purposes of this discussion a modern conductor will mean a composite consisting of many continuous fine strands or filaments of a superconducting material embedded in a matrix of one or more normally conducting metals.

The paper is in two parts. The first part briefly describes the "state of the art" in the NbTi alloy composites and what can be expected from them in the near future, and the second part summarizes the potential of other superconductors which might compete with NbTi in magnet applications.

2. NbTi Composites, State of the Art

It is assumed that the reader is aware of the advantages of twisted multifilamentary composites and no attempt will be made to present the theory which has been described so well by Smith and his associates of the Rutherford High Energy Laboratory.[1] One important concept concerning the relationship between the filament size required for "intrinsic stability" and the critical temperature should be mentioned, however. This is illustrated in Fig. 1, where x represents the filament size and s the specific heat of the superconductor in a composite conductor. It is obvious from Fig. 1 that the quantity T_o is approximately equal to the excess of the critical temperature over the operating temperature (usually 4.2 K). Since the critical temperature, T_c, is one of the parameters that new materials could increase, it is worth noting that this would improve the stability for filaments of a given size. Conversely, an increase in the critical current, J_c, another desirable feature of a new material, would lead to reduced stability or require smaller filaments.

$$X < \frac{\sqrt{10^9 \pi S T_o}}{4 J_c}$$

$$T_o = \frac{J_c}{-\frac{dJ_c}{dT}}$$

ADIABATIC STABILITY

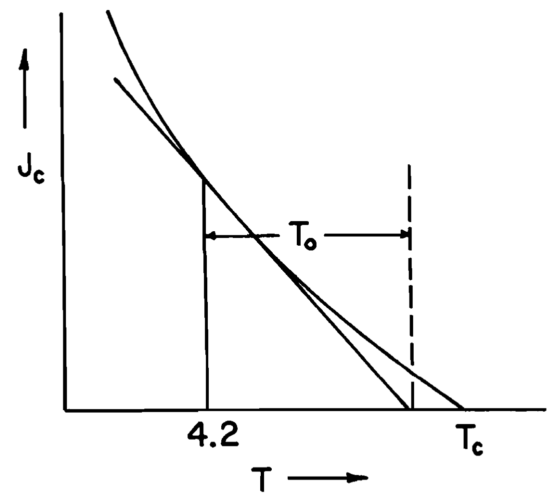

Fig. 1. Stability criterion. For filament diameters, x, smaller than a certain size the conductor will be "intrinsically stable." In this expression s is the specific heat of the superconductor. From the diagram it is apparent that the quantity T_o is approximately equal to the difference between the critical temperature, T_c, and the operating temperature (usually 4.2 K).

2.1. Current Density

The current density obtainable in NbTi composites has been steadily improving over the last five years. Variations in the fabrication procedures have led to materials which have a reduced J_c at low fields, where it is not needed and leads to excessive ac losses, and improved current density at high fields. This is illustrated in Fig. 2, where the current density in the superconductor is plotted as a function of magnetic field for two conductors of different vintages. Despite the recent improvements in the J_c of NbTi composites, there appears to be an upper limit. Discussions with manufacturers indicate that a value of approximately 3×10^5 A/cm^2 at 40 kG is about as high as J_c can be pushed in usable NbTi conductors.

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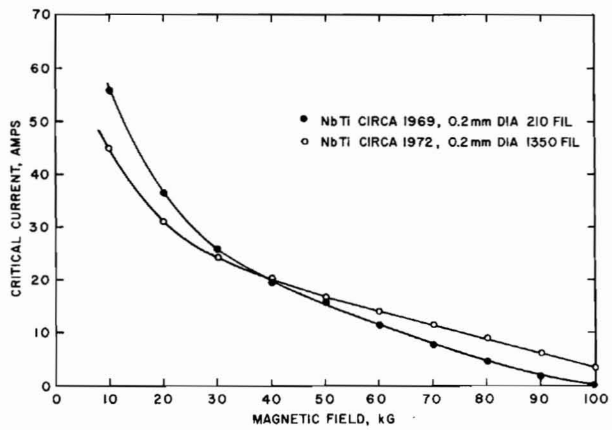

Fig. 2. Comparison of "old" and "new" NbTi conductors. Improvements in manufacturing technique have reduced the low field current and increased the high field current.

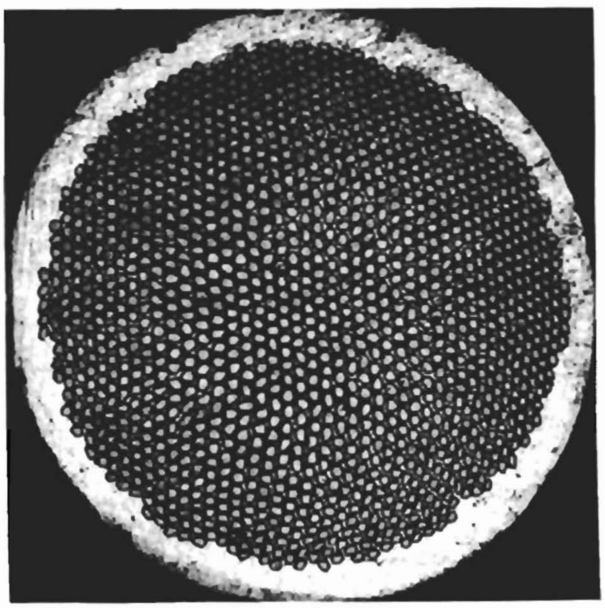

Fig. 3. Microphotograph of NbTi-copper composite. The over-all diameter of the wire is 200 μ. There are 1350 filaments of 4 μ diameter.

Currently available composites have a J_c of 2×10^5 A/cm^2 at this field.

2.2. Filament Size

One of the most notable features of NbTi alloys is their great ductility. As we shall see, this property is not shared by other attractive superconducting materials and is the principal reason that NbTi technology has progressed so rapidly in recent years. Because of the ductility of this alloy and the ductility of the most common matrix material, copper, it has been possible to produce composites with very fine filaments.

Figure 3 is a microphotograph of a composite containing about 1300 filaments of only 4 μ diameter. In this case the over-all diameter of the conductor is only 200 μ. Filament sizes this small are considerably below the size required for stability, but are needed in applications where the ac losses are important or where the effects of magnetization currents must be minimized. There does not appear to be a technical limit to filament size (material has been drawn with filaments only 1 μ in diameter) but practical limitations on the number of filaments in the conductor usually limit the size to at least a few microns.

2.3. Onset of Resistivity

For superconducting wires with large cores, the transition to the normal state usually occurs at a well-defined current and curves of J_c against magnetic field can be drawn unambiguously. As the size of the filaments is reduced, however, the appearance of voltage (and thus "effective" resistivity) occurs gradually as the current is increased. Thus curves of critical current against magnetic field can be drawn for different over-all effective resistivities, as shown in Fig. 4. It has become accepted practice to use an effective resistivity of 10^{-12} Ω·cm for specifying short

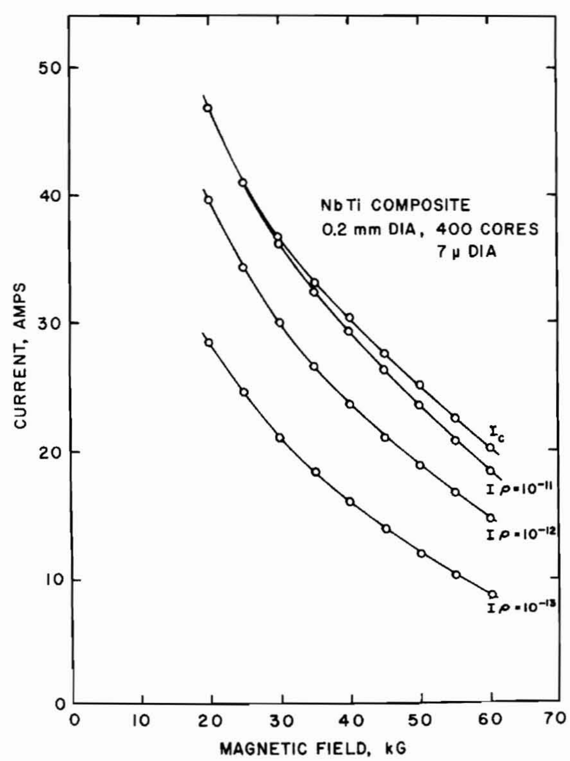

Fig. 4. The current plotted against magnetic field for a typical composite. The curves are for different over-all effective resistivities. The curve labeled I_c is the current at which the voltage across the test sample is no longer stable with time and is thus the quench current.

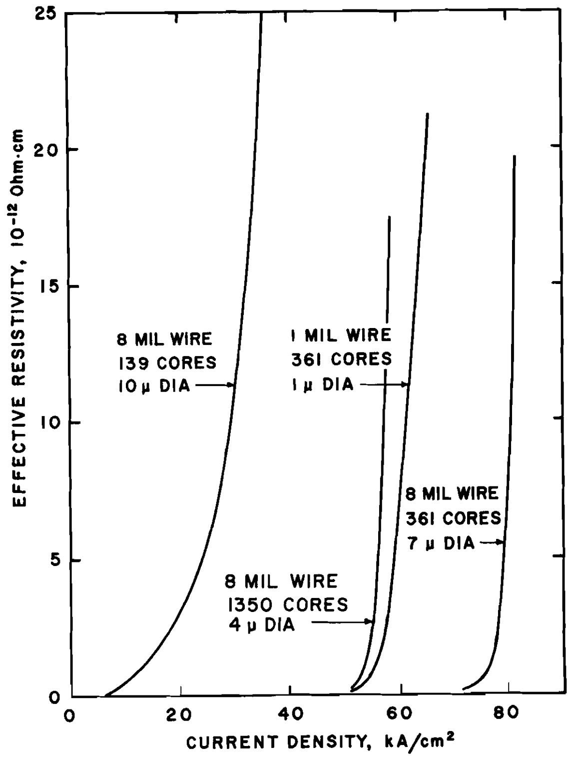

Fig. 5. The effective resistivity plotted against over-all current density for several NbTi conductors measured at 40 kG. All samples are from the same manufacturer.

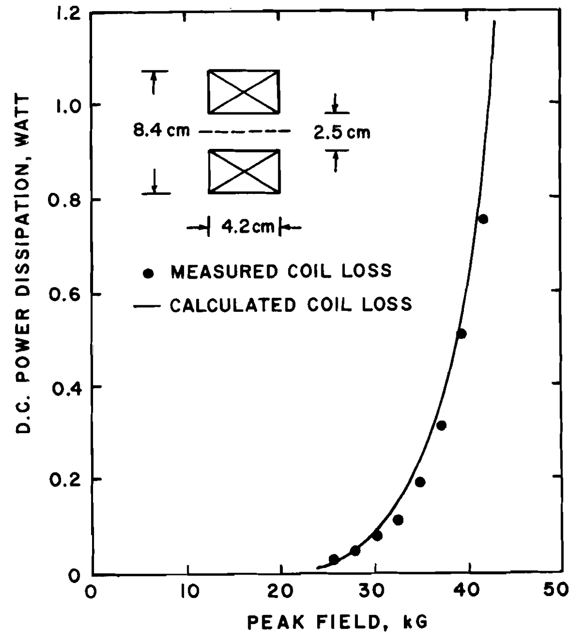

Fig. 6. Losses under dc conditions for a small solenoid as a function of field. The calculated points were obtained by numerically integrating short sample data over the volume of the coil.

sample critical current in very fine filamentary wire. This gradual onset of resistivity is thought to be due to physical or metallurgical "necks" or narrow spots along the filaments. Conductor manufacturers have learned to control this behavior by their processing and can produce very good characteristics as shown for some of the samples of Fig. 5. All the conductors shown in Fig. 5 were made by the same company and some idea of the variety of possibilities can be gained from this diagram. There does not seem to be any correlation between filament size and the onset of resistivity as some of the best conductors in Fig. 5 have very fine filaments. The result of this effective resistivity is the appearance of losses under dc conditions. The losses calculated from the onset of resistivity profiles of short samples are compared to the actual measured losses of a small solenoid made from the same material in Fig. 6. The agreement is striking and illustrates the importance of good conductor characteristics. Needless to say, such losses would play havoc with "persistent mode" operation. While the field distribution in a solenoid is such that dc losses are minimized, this is not true of dipole magnets and very good material is required for acceptable operation.

3. Double Composites

The small wires containing many filaments are usually combined in groups in the form of cables or braids for use in magnet construction with the individual wires insulated from each other by an organic coating. In recent years a further development in conductors has taken place with the production of "double composites." Conductors of this type consist of arrays of filaments combined to form a larger conductor with many thousands of filaments. A conductor of this type with a more or less round cross section has been developed by I.M.I. in conjunction with Rutherford[2] and is described elsewhere in these Proceedings. A second ribbon-type conductor has been developed at BNL.[3] In this case, many small wires each containing several hundred filaments are braided to form a flat ribbon which is then filled with a secondary matrix of soft metal which is heat treated to increase the interwire resistance. A microphotograph of this type of conductor is shown in Fig. 7.

4. New Conductors

Now that we have seen the properties of the conductors that can be produced with NbTi let us look at the possible replacements for this alloy and evaluate their advantages and shortcomings. Table I is a list of superconducting materials which have at least one critical parameter that is greater than the corresponding parameter for NbTi.

TABLE I. The critical parameters of some interesting high field materials.

Superconductor	Crystal Structure	T_c (K)	H_{c2} (4.2 K) (kG)	J_c (4.2 K, 40 kG) (10^5 A/cm^2)	J_c (4.2 K, 100 kG) (10^5 A/cm^2
NbTi	BCC	10	120	3	0.3
Nb_3Sn	A15	18	230	20	5
V_3Ga	A15	15	220	10	4
V_3Si	A15	17	230	3	0.5
Nb_3Al	A15	19	~ 300	?	?
Nb_3Ga	A15	20	~ 200	?	?
Nb_3(Al,Ge)	A15	21	400	?	3 (Ref. 4)
V_2(Hf,Zr)	C15	10	240	5	2 (Ref. 5)
NbN	NaCl	18	~ 200	?	?

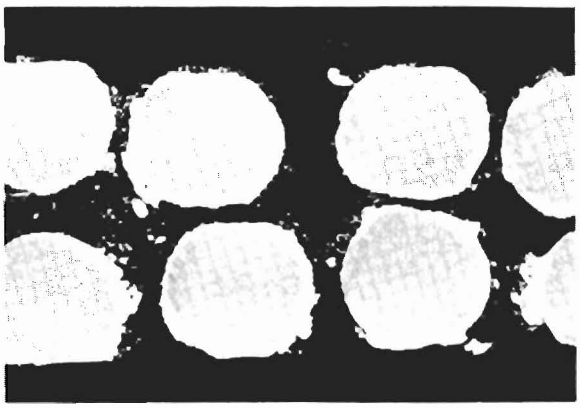

Fig. 7. A double composite braid of multifilamentary wires in an indium-thallium matrix. The microphotograph shows only a section of the braid which is 0.5 mm thick and 1.6 cm wide. The dark grey material between the wires is a high resistivity intermetallic formed by heat treatment after braiding.

The two most promising candidates in Table I are the well-known compounds Nb_3Sn and V_3Ga, both of which are commercially available in the form of wide-ribbon conductors. The other A15 compounds have high critical temperatures and high critical fields but have not, as yet, been fabricated into conductors suitable for magnet applications. The vanadium-hafnium-zirconium material is one representative of a whole family of materials of this type which have been studied by Tachikawa and his associates in Japan.[5] These materials have a C15 crystal structure and may be more ductile than the A15 compounds although they have rather low values of T_c.

4.1. Solid-State Diffusion

The basic problem which arises in trying to produce multifilamentary composites from the compound superconductors is the very low ductility of such compounds. A method which circumvents this difficulty has been developed and successfully used to produce both Nb_3Sn[6] and V_3Ga[7,5] composites. The lack of ductility is avoided by not forming the superconducting compound until all the extrusion and drawing steps have been completed. Billets consisting of niobium or vanadium rods embedded in a tin-copper or gallium-copper matrix are formed in much the same way as the conventional NbTi in copper billets. After extrusion and drawing to the final dimensions, the wire is heat-treated and tin or gallium from the bronze matrix diffuses into the core material to form fine filaments of Nb_3Sn or

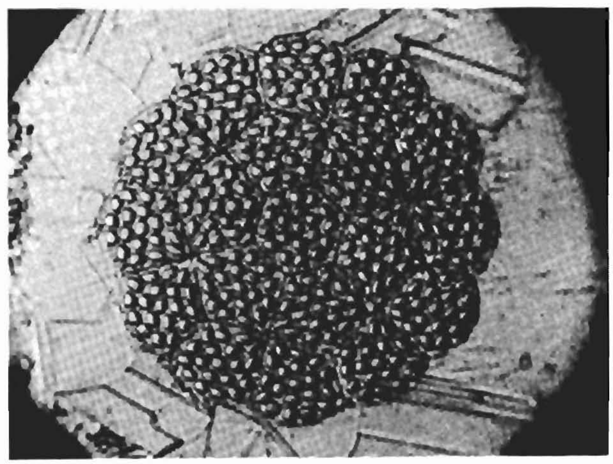

Fig. 8. V_3Ga composite formed by heat-treating vanadium filaments in a gallium bronze matrix. The conductor is 200 μ over-all diameter and contains 361 cores of 4 μ diameter. Unreacted vanadium is visible at the center of each core.

V_3Ga. A microphotograph of a V_3Ga composite containing 361, 4 μ cores is shown in Fig. 8. Axial twisting of the composite is usually done before the heat treatment which forms the high critical temperature superconductor. This procedure has been tried on the first five A15 compounds of Table I. V_3Si was also found to form[8] but Nb_3Al and Nb_3Ga would not. Because both niobium and vanadium are superconductors and have quite high critical currents when heavily cold-worked, it is possible to investigate the uniformity of the filaments before heat treatment by measuring the current-voltage properties of the initial conductor which is a low field composite. The formation temperature is usually lower than that used for tape conductors. For Nb_3Sn the optimum temperature is 700°C and for V_3Ga about 650°C.

4.2. External Diffusion

There is, however, one drawback to the procedure outlined above. The bronze matrix material is easily work-hardened and must be annealed repeatedly during the drawing operations. This is expensive and time consuming. A new method has been developed which eliminates the annealing steps.[9] In this technique billets consisting of rods of core material (i.e., niobium) in a pure copper matrix are reduced to the final configuration. No annealing is required because of the high ductility of niobium and copper. At final size the wire is coated with the second component (i.e., tin) by a dipping process and the tin is diffused into the copper at a low temperature (~ 400°C). The amount of tin can be regulated by the bath temperature and the number of coating passes. This procedure is outlined in Fig. 9 where it is contrasted with the bronze technique. A microphotograph of a Nb_3Sn composite made in this way is shown in Fig. 10. This process can also be used to make V_3Ga composites.

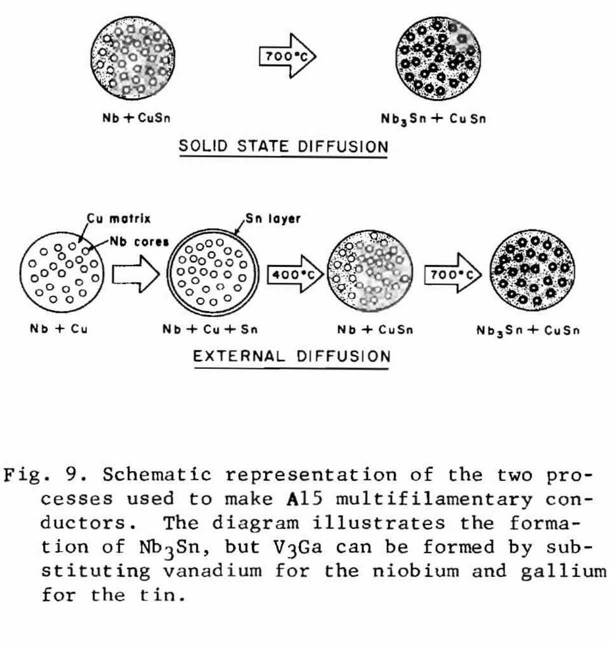

Fig. 9. Schematic representation of the two processes used to make A15 multifilamentary conductors. The diagram illustrates the formation of Nb_3Sn, but V_3Ga can be formed by substituting vanadium for the niobium and gallium for the tin.

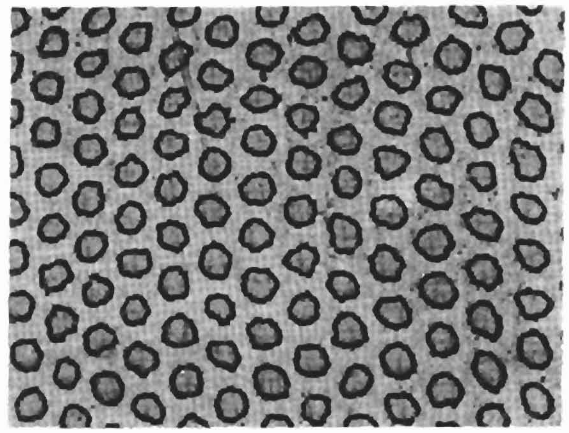

Fig. 10. Microphotograph of a portion of a Nb_3Sn composite made by the external diffusion technique. The Nb_3Sn can be seen as a thin layer on the niobium cores. The over-all size of this wire is 200 μ and the niobium cores are each 5 μ in diameter.

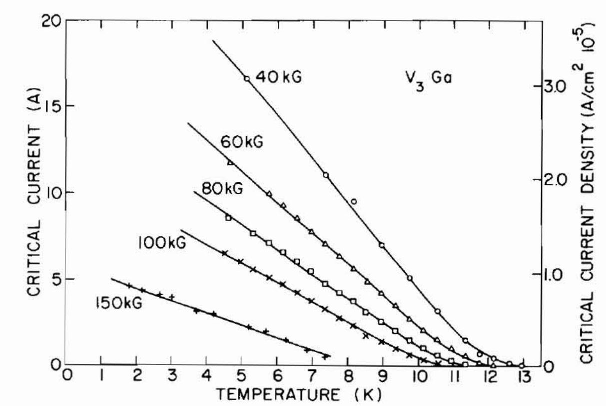

Fig. 11. The temperature dependence of the critical current for a V_3Ga composite.[10]

4.3. Properties of New Composites

The critical temperatures of the A15 composites are usually within one-half degree of the bulk value and the temperature dependence of the critical current is quite linear as shown in Fig. 11. The current density of the superconducting filaments is very high although it is dependent on the layer thickness, the highest values being obtained for the thinnest layers. This feature is compatible with the filamentary form, however, since the layers are by necessity only a few microns thick. The matrix resistivity is substantially higher than that of pure copper and while this is attractive from the ac loss point of view it can lead to unstable performance. In this respect gallium-bronze is better than tin-bronze by approximately an order of magnitude and has a resistivity at 4.2 K approximately equal to that of copper at room temperature. The onset of resistivity in the new

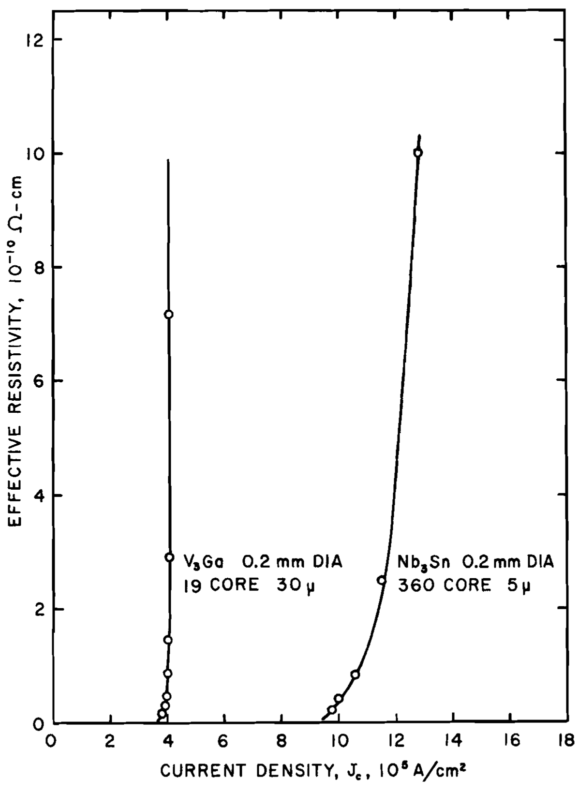

Fig. 12. The effective resistivity as a function of current density in the superconductor for typical samples of Nb_3Sn and V_3Ga composites. The measurements were made at 40 kG.

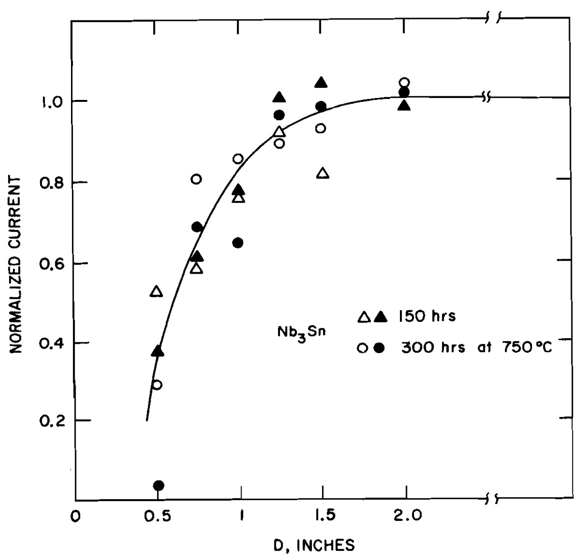

Fig. 13. The effect of bending on Nb_3Sn composites.[9] Short samples are bent around a mandrel, straightened and then remeasured. This procedure is repeated for successively smaller mandrels to produce this curve.

composites is similar to that observed in the most conventional composites as illustrated in Fig. 12.

The great disadvantage of this type of conductor is its limited ductility. Even though this has been circumvented in the production of the conductor it becomes a problem again when the conductor is bent during the construction of devices. Figure 13 shows the effect of bending on a V_3Ga composite of 0.2 mm over-all diameter. While a minimum bending radius of 1 or 2 cm may be permissible for small solenoid windings, it is not compatible with the rather brutal treatment wires are subjected to in a cabling or braiding operation. It may prove possible to "heal" the material after braiding or even after magnet winding by a short low temperature heat treatment, but this is not a desirable feature. Another approach could be to delay the formation of the compound until the "double composite" stage where the conductor is already large and hence subject to less bending.

5. Conclusions

The development of a replacement for the very sophisticated NbTi composites now available will not be an easy task. The potential for greater current density and higher fields is considerable, however, and as designers of devices begin to reach the inherent limitations of NbTi, the pressure to perfect new conductors will increase. The most serious problem with new composites is a lack of "effective" ductility. This can probably be reduced to manageable proportions by additional development.

6. Acknowledgements

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