COMPOSITE MATERIALS*

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This talk will be a briefing on the "state of the art" as it is known by the author. Most of the information acquired with respect to fabrication was obtained while the author was a "Senior Research Physicist" at Atomics International, where metallurgist Gordon Chase and the author worked on alloy development of TiNb as a superconductor. A small fraction of the metallurgical work presented here was performed after the author's arrival at Brookhaven.

There are certain criteria which will be applied to a material to rate its usefulness. (These are by no means all the criteria that are relevant, e.g., upper critical field, critical temperature, etc.) These criteria are:

1) The critical current density for the superconductor plus normal material [Cu, Ag, and/or mechanical support material, if needed, etc. (maximum)] vs applied perpendicular magnetic field.
2) The magnetization of the materials [this is a function of J_c ($H_{applied}$) and geometry, thermal and electrical environment (minimum)].
3) Flux jump stability [this parameter is a function of mechanical rigidity and criteria 1) and 2) (maximum)].
4) Reproducibility of these properties with a given production process:
    a) For small quantities and all sizes of conductors.
    b) For larger quantities and all sizes of conductors.

The materials used in the experiments were in most cases commercially available samples with known metallurgical histories. Some were obtained to test from users, who had them submitted by the producers for a particular contract. Samples tested originated from the following manufacturers: Atomics International, Avco, Cryomagnetics, General Electric, Radio Corporation of America, and Supercon. This paper will not refer to a sample by its producer, because in certain cases a great deal of time was spent to find a piece of the material which displayed a desired characteristic, be it an asset or a detriment. The materials tested were Nb_3Sn and various alloys of TiNb. Most of the fabrication techniques with respect to composites where applicable to TiNb alloys are usually applicable to NbZr alloys as well.

The composites discussed will be of three different types. There will be some overlap, of course. These types are:

I. Cable (strands):
    A. Cable composed of a nonstabilized individual superconductor, stranded with and soldered to stabilizing, high-conductivity normal material (e.g., annealed Cu). (See Fig. 1.)

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*Work performed under the auspices of the U.S. Atomic Energy Commission.

B. Cable composed of individually stabilized wires, where the normal metal jacket is thick enough to enable the entire superconductor to go into the normal state, and the current to divert through the high-conductivity jacket without sufficient heat being generated to cause the normal region to propagate to the rest of the conductor, stranded and soldered together to produce a high-current cable. Actually, this type can be run under partially stabilized or fully stabilized conditions quite reliably.

II. The filamentary or strand composite [which will include from a few to several hundred filaments (≤ 0.01 cm in diameter) or strands (≥ 0.01 cm in diameter)]:

The superconductor is located as filaments or strands in (a) a metallurgically, or (b) a mechanically-bonded, high-conductivity metal matrix. There may be sufficient high-conductivity metal present to stabilize the total composite current or a fraction thereof. (See Fig. 2.)

III. A multilayered composite, which might be fabricated by the following processes:

A. Vapor deposition (normally a ribbon geometry). (See Fig. 3.)

B. Soldered layers (normally a ribbon geometry).

C. Plating.

D. Diffusion (or reacted). (See Fig. 4.)

E. Casting (normally a ribbon geometry).

F. Any combination of the above.

The actual fabrication of the ductile alloys (e.g., TiNb) that would go into types I, II, III-B, III-C, and III-E of the composites will be evaluated with respect to criteria 1), 2), and 3).

There are various metallurgical processes for a given alloy which can optimize criterion 1), i.e., obtain the maximum critical transport supercurrent for a given perpendicular applied field. The process usually consists of some schedule of heat treatment and cold work (% area reduction). Both of these processes are thought to provide pinning sites in the alloy.[1,2]

The yield point and fracture point start to coincide and the hardness increases as the critical current of these alloys increases in the region where the applied fields are in excess of that required to totally penetrate the superconductor with flux. Therefore, the difficulty of further fabrication or handling of the alloys in this metallurgical state, where they would have a high current density, is greatly increased.

The mechanical parameters and the flux jump stability of the sample are quite different depending on whether the last step in the process is cold work (reduction) or heat treatment.

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1. J.B. Vetrano and R.W. Boom, J. Appl. Phys. 36, 1179 (1965).

2. A.D. McInturff et al., J. Appl. Phys. 38, 524 (1967).

A superconducting sample, whose critical current density is not maximized with respect to the variation of the last step in the fabrication process (e.g., cold work or heat treatment time) will in general not undergo flux jumps at fields in excess of the penetration field if the bond (metallurgical or mechanical) between the alloy and the high-conductivity material (thermal and/or electrical) is good (low resistance). Even if the sample undergoes flux jumps in that region, the flux jumps will tend to be localized and not occur across the entire conductor.

If samples are being mapped for a maximum in the critical transport current density at a given perpendicular field H_a [where $H_a \gg H^*$ (field of complete magnetic flux penetration) as shown in Fig. 5] as a function of various values for the last step in fabrication (e.g., % cold work), certain generalizations may be made about the resulting superconductor. These generalizations, of course, are subject to the bond quality. Assume that it is good (high conductivity, thermal and/or electrical). The samples which lie to the left of the peak will either not undergo flux jumps, or if they do, the jumps will tend to be localized and less numerous. The samples which lie on the right side of the peak (Fig. 5) will have flux jumps which are both numerous and catastrophic.

There are various possibilities that will cause flux jump instability to increase in frequency and/or magnitude:

1) A diffusion layer of the superconductor into the high-conductivity surroundings, causing a resistive bond at very low applied fields (either excess heat treat temperature and/or time). (A very thick layer of alloys and/or compounds formed by the superconducting alloy and the interdiffusion and reaction of the high-conductivity matrix.)
2) A mechanical breaking of the bond.
3) Physical break-up of the superconductor because of brittleness.
4) Cold-working of the superconductor to a high degree as the last step.

It should be noted here that although one can usually obtain slightly higher current densities for short samples with cold work as the last step in fabrication, the resulting superconductor is, in general, much more flux-jump unstable, the reason being that $\partial J_c(H)/\partial H$ has a larger magnitude for cold-worked samples in general. Such samples can be used reliably only in composites I-A, II-B (with a lower conductivity jacket, e.g., cold-worked Cu), and III-B, which tends to negate the higher current density in the windings due to lower over-all current densities of the resulting composite. The reproducibility of the desired characteristic in large quantities (or even the production of long, continuous lengths) is much more difficult. The chances of mechanically breaking the superconductor to high-conductivity metal bond is greater for this type of fabrication.

Heat treatment, as a last step in a process, can result in diffusion layers being formed between the superconductor and the high-conductivity material. This is usually the result of excessive heat treat temperature in an effort to obtain a maximum $J_c(H)$ in a desirably (from a production cost standpoint) short time.

It should be noted that even with vapor-deposited superconductors (Nb_3Sn or TiNb) that have been plated or vapor-deposited over with a high-conductivity material, a heat treatment which metallurgically bonds the components together will greatly affect the flux-jump stability (see Fig. 6).

It is obvious from the figures that the high-conductivity matrix affects the behavior of the superconductor drastically. This point will be expanded in the Ac Session paper.

Geometry is probably the next most important factor to be considered. In Fig. 7 an extreme example (a thin sheet geometry of Nb_3Sn) is taken with the upper diagram representing the hysteresis curve for 0.97 cm width, the middle, 0.6 cm width, and the lower, 0.3 cm width. Data for TiNb on a similar geometry displayed the same behavior. No matter how good the mechanical and thermal environment, if the geometry is poor the performance will be likewise.

When size independence experiments[2] were performed and found to be valid, two large conductors were designed and fabricated. It was found that, although they had extremely high critical currents during short sample tests with large cold-welded leads on them, a magnet section that was fabricated with them was very noisy (large number of flux jumps), and great care had to be taken during the charging cycle during which there was a large helium boil-off.[3] This behavior was due to the flux-jump instability in the particular geometry chosen, namely that of a very large superconductor (which of course is a very cheap conductor to fabricate). This problem can be partially remedied by applying a saturation field with the outer sections of the magnet. The effectiveness of the saturation field results from the fact that most of the flux jumps occur at fields less than 10 kG in Ti22a/oNb. There have been samples fabricated as large as 0.170 cm. Although with large leads cold-welded to them and with a low resistance shunt across them, these large samples would carry very high current densities (up to short sample characteristics of smaller samples), they were flux-jump unstable. The effects of this instability can be remedied with massive amounts of high-conductivity material in good electrical contact with the superconductor (e.g., I-B, II, III-A, III-E). The jumps will still occur, but the magnet will not quench, a relatively poor design in light of up-to-date information.

Now to recapitulate the discussion, an outline is presented which uses the various composites as the division basis and the performance standards as subdivisions.

I. Stranded cable — materials normally used are a ductile alloy of TiNb or NbZr potted in a solder.

   A. Composed of nonstabilized superconductors.

      1. The critical current density vs applied magnetic field of the superconductors can be quite high, but by the time the stabilizing or partially stabilizing high-conductivity material and solder are added, the over-all current density is quite a bit lower, $\approx 10^4 \rightarrow 10^3$.

      2. Magnetization of the composite is completely a function of the size of the superconductors used for a given cross section of superconductor desired.

      3. Flux-jump stability of the composite is a function of the impregnation of the cable and that of the individual conductors (geometry, metallurgical history, etc.).

   B. Composed of stabilized superconductors.

      1. Critical current density vs applied field is good. After a number of these stabilized wires are stranded together their combined current density is less markedly reduced, $\approx 10^4$.

      2. The magnetization of the composite is determined by the size of the individual superconductors for a given cross section of superconductor desired (these are normally twisted).

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[3] H. Brechna, private communication.

3. Flux-jump stability is no longer a function of the impregnation of the cable, only that of the individual conductor jacket (geometry, metallurgical history, etc.). I-B is usually much more stable with smaller losses during charging of a coil than I-A. Because of the greater flux-jump stability, the smaller diameter I-B types can more readily be run in a partially stabilized configuration than the smaller diameter I-A types.

II. Filamentary or strand composite — materials normally used are the ductile alloys (e.g., TiNb, NbZr), but if a high-temperature, high-conductivity material were available with slow Sn diffusion rate — slower than Nb — then the intermetallic compounds such as Nb_3Sn with their higher H_{c2} and T_c could be used. Normally, the last step in fabrication is a heat treatment.

A. Metallurgically bonded (usually an extruded plug in a soft-annealed state and subsequently drawn and then heat treated).

1. The critical current density is at an optimum for any configuration (geometry) that is desired, be it filamentary or strands. It may be totally stabilized or only partially. The ability to reproduce short-sample characteristics is excellent in such a process.

2. The magnetization curves are governed by the individual size of the filaments or strands and their proximity to one another. [Enhancement factors of three have been found by proximities of the order of filament diameters (0.003 cm) in samples 7 cm long.] The ratio of the magnitude of the magnetization of the composite to a given total cross section for the superconductor may be minimized here by variation of the filament size and various properties of the surrounding matrix.

3. The flux-jump stability, where a heat treatment is picked to give optimum conductivity of the matrix, optimum bond of matrix to superconductor, and high $J_c(H_{applied})$, can be maximized by minimizing the absolute value of $\partial J_c(H)/\partial H_T$ const. and $\partial J_c(T)/\partial T_H$ const.

B. Mechanically bonded (same as II-A above).

III. Multilayer composite (usually ribbons). The intermetallic compounds such as Nb_3Sn are normally commercially made in this form, but the ductile alloys may also be fabricated in this form.

A. Vapor deposition — evaporation process is versatile and allows production of composite conductors that cannot be made otherwise. The process is most efficient for depositions ≥ 0.003 cm thick over large areas, for example 0.003 cm of TiNb may be deposited on 5 to 15 cm wide strips at the rate of 120 m/h using 30 kW for evaporation.

1. Critical current densities vs applied field are good although those achieved so far seem to be slightly less than those obtained with other methods of fabrication (this observation is for ductile alloys only).

2. Magnetization curves for normal vapor-deposited composites tend to be high due to their width (perpendicular magnetic field). In some cases the samples are in the form of a flattened-out cylinder. This can be remedied somewhat by subdivision.

3. Flux-jump stability is not optimum here, but this is a function of the normal geometry (ribbon-like), not the process. It is critical in the thin disk configuration.

B. Soldered layers. Here the individual superconductor is soldered into a stabilizing or partially stabilizing matrix.

   1. Critical current density in the superconductor may be quite high, but in the entire composite it is considerably reduced for complete stability. The process is normally difficult for more than a few such layers.

   2. Magnetization of the composite is usually that of the superconductor. Here again the geometry is usually poor (wide one) and the magnetization is quite large.

   3. The flux-jump stability for this type is not optimum due to normal geometry. It also suffers from one more drawback than III-A, namely that of impregnation of the composite with solder, and hence, the possibility of voids.

C. Plated composite. This is a process normally used to give partial stability to the material (adding on high-conductivity material), and results mainly in aiding criterion 3), "greater flux-jump stability." This process does not lend itself readily to the fabrication of very thick layers.

   1. Same as III-A-1.

   2. Same as III-A-2.

   3. Same as III-A-3.

D. Diffusion composite. The conductors normally fabricated by this process are in the form of a ribbon of one of the constituents of the desired superconductor, which is coated by the other constituent or placed in physical contact with the other and then reacted together in a diffusion process. The resulting material is normally one of the intermetallic compounds, e.g. Nb_3Sn. A drawback to this procedure is that the resulting composites are generally weak mechanically.

   1. Critical current densities of the over-all composite are usually quite high in this process.

   2. The magnetization is the same as III-A-2, except that any of the unreacted Nb ribbon left adds to the low field magnetization of the sample. (Since this is also the mechanical strength member, a compromise in size must be chosen.)

   3. The flux-jump stability seems slightly increased over III-A. This additional stability may be due to the presence of the Nb providing low field shielding of the flux.

E. "Casting" of a composite is an idea that has been around a long time because it would be a cheap method of fabrication, but to the best of the author's knowledge the major difficulties of temperature vs superconducting bond problems have not been worked out.

   1. Critical current densities are very low.

   2. Magnetization is unknown.

   3. Flux-jump stability is unknown.

F. Combination of the above processes resulting in a composite. The properties would be a combination of the above.

Examples of all of the criteria have been shown previously in the figures except criterion 1). Figure 8 shows typical $J_c(H_{applied})$ vs $H_{perpendicular}$ curves for various materials now available.

In conclusion allow me to state a personal observation, first of what would be optimum from the standpoint of dc and ac applications based on what is presently known, and second, what probably will be the future course of action.

First, I believe and a lot of other people with me believe it to be obvious that multifilament composites containing only the superconductor in appropriate filament size with sufficient amounts of high-conductivity metal to insure flux-jump stability, and enough high-conductivity metal to allow several stable filament superconductors to undergo normal transitions and return to the superconducting state, are the answer for both ac and dc applications. I do not believe that it is necessary to go to smaller filaments than 30-40 μ, and indeed maybe not even that small when one takes into account the proximity effects of the magnetization of the composites, unless one is able through the introduction of resistance to decouple the strands or filaments, especially in light of calculations presented by various speakers[4-7] at this Summer Study. If a high-temperature, high-conductivity material with a very slow Sn diffusion rate could be developed, the multifilament composite could employ Nb_3Sn as well as the ductile TiNb and NbZr alloys. But for the near future probably scribed layers of either vapor-deposited or diffusion-processed Nb_3Sn will be available.

Upon evaluation of papers presented by Wipf,[4] Hart,[5] Smith,[6] and Stekly[7] during the weeks of the Summer Study, the conclusions of the author were slightly modified in that perhaps a highly resistive diffusion layer, that is, a very small thermal conduction barrier, might greatly reduce the coupling in twisted multifilament composites having filament diameters around 0.003 cm.

ACKNOWLEDGEMENTS

The author wishes to thank G.H. Morgan for his helpful comments on this paper, and W.B. Sampson and R.B. Britton for the use of their magnets in these experiments.

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[4] S.L. Wipf, these Proceedings, p. 511.

[5] H.R. Hart, ibid., p. 571.

[6] P.F. Smith, ibid., p. 913.

[7] Z.J.J. Stekly, ibid., p. 748.

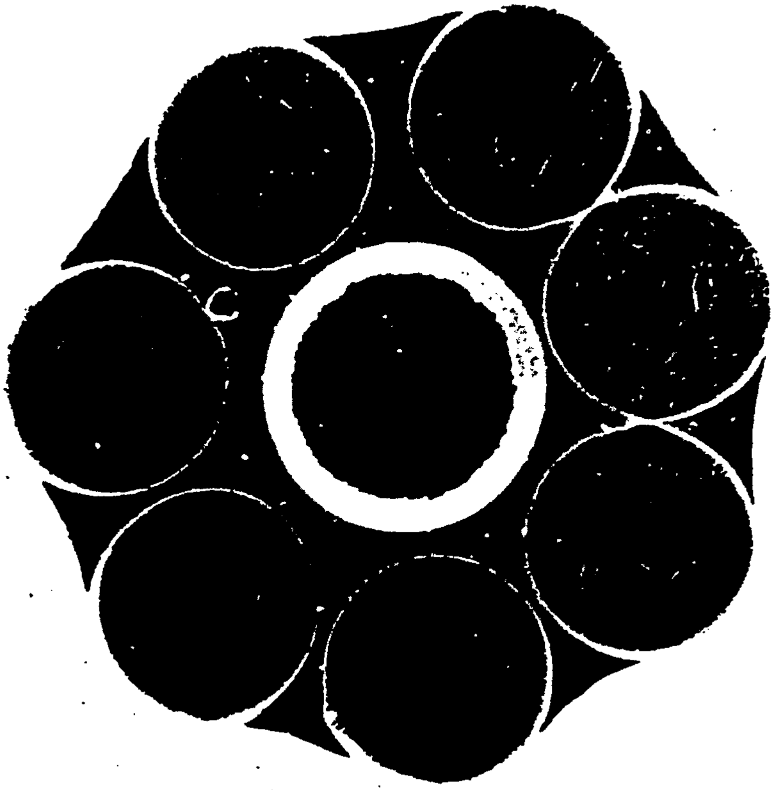

Fig. 1. Micrograph of a stranded cable consisting of a Ti22a/oNb copper-coated center strand (0.0508 cm diameter) with six highly annealed copper strands (0.0508 cm diameter) around it, potted in a SnAg solder.

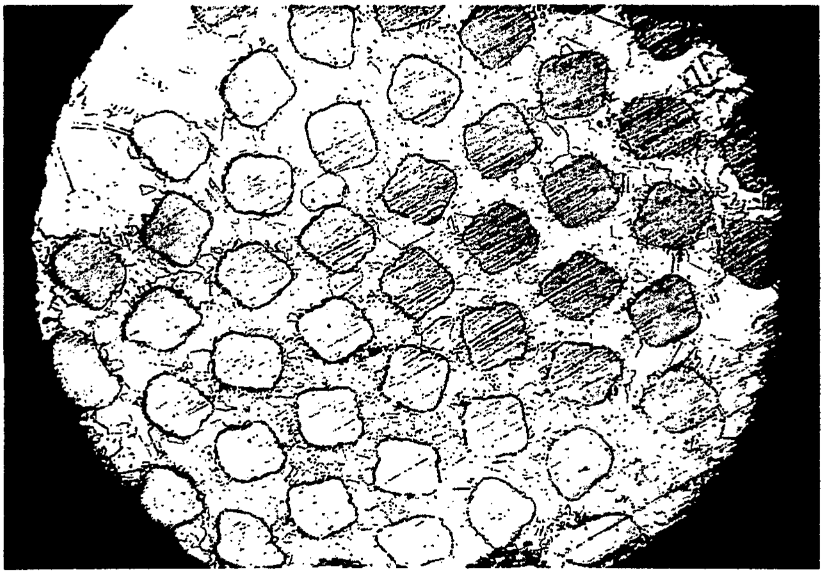

Fig. 2. Micrograph of a multifilament conductor (0.0508 cm diameter) containing 52 TiNb filaments (individually ≈ 0.0038 cm in diameter) in a highly annealed copper matrix.

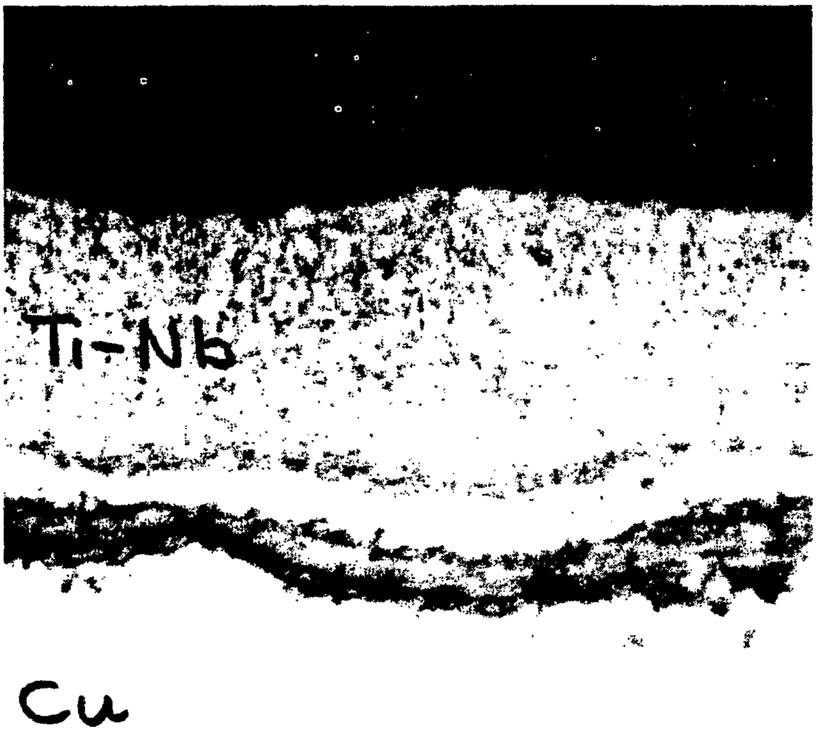

Fig. 3. Micrograph of a multilayer composite in which the superconductor was obtained by vapor deposition or a substrate (Cu).

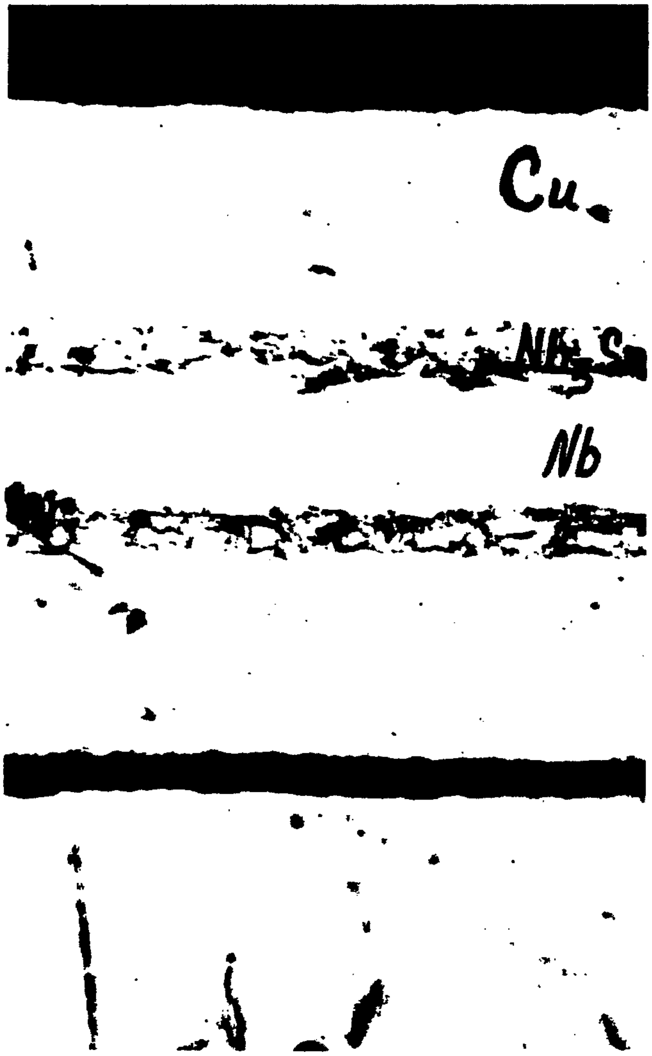

Fig. 4. Micrograph of a multilayer composite in which the superconductor was obtained by diffusing a Sn solder layer into a Nb ribbon and then copper-plating.

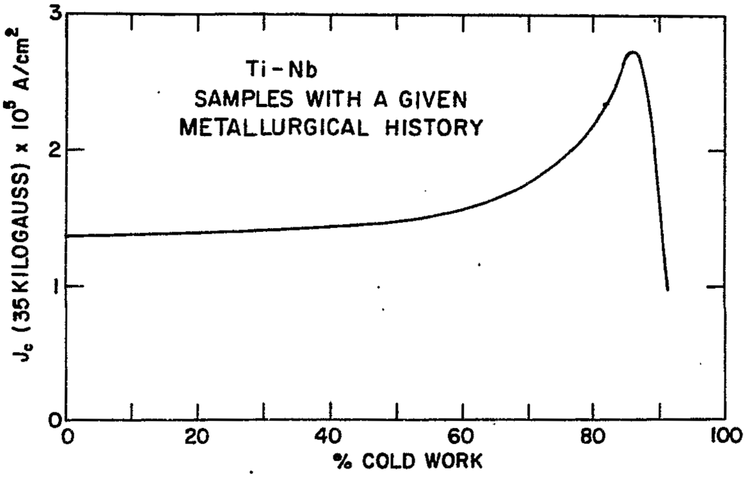

Fig. 5. A map of one of the various metallurgical parameters that are varied to obtain a given superconductor with various desired properties (these are data obtained by the author for a test sample).

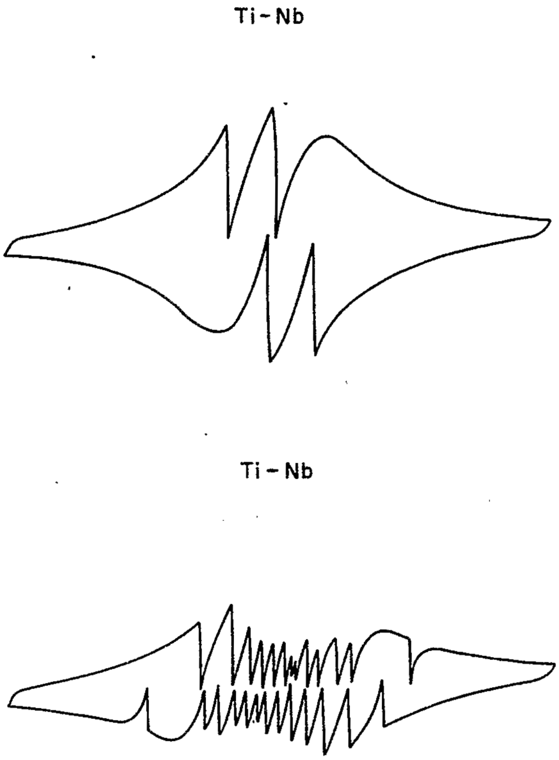

Fig. 6. Tracings of an x-y recorder for $\overline{M}$ on the y-input and $\overline{B}$ on the x-input ($H_{max} = \pm 40$ kG). The upper curve is for a sample of Ti48a/oNb with an excellent bond between superconductor and copper. The lower curve represents an identical sample except the bond between superconductor and copper was very resistive and mechanically weak. These samples had the same $J_c(H_a)$ (perpendicular) curves when the copper was etched off and the samples were sand-blasted and indium-tinned and then soldered to large copper pads for transport current connections.

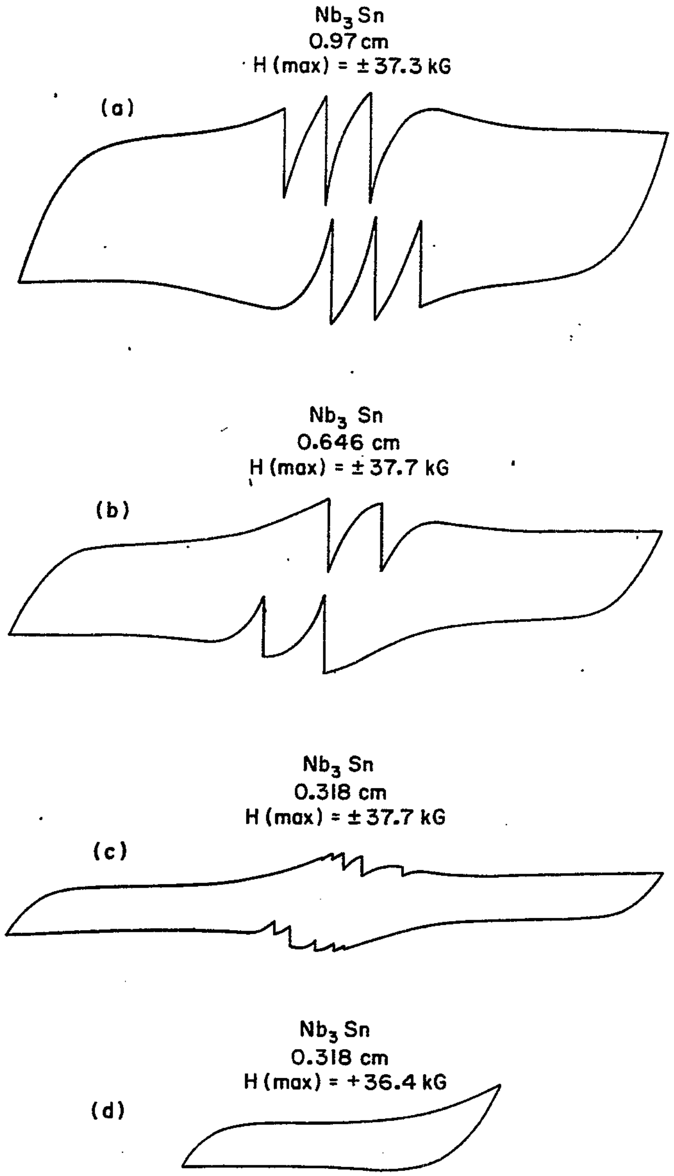

Fig. 7. Tracings of an x-y recorder for $\overline{M}$ on the y-input and $\overline{B}$ on the x-input ($|H_{max}|$) $\cong$ 40 kG. In curves (a), (b), and (c) the field $\overline{H}$ has both positive and negative values. In curve (d), $\overline{H}$ is only negative. Curves (a), (b), and (c) represent variations of the smallest perpendicular width for a ribbon sample, with the field $\overline{H}$ perpendicular to the flat side.

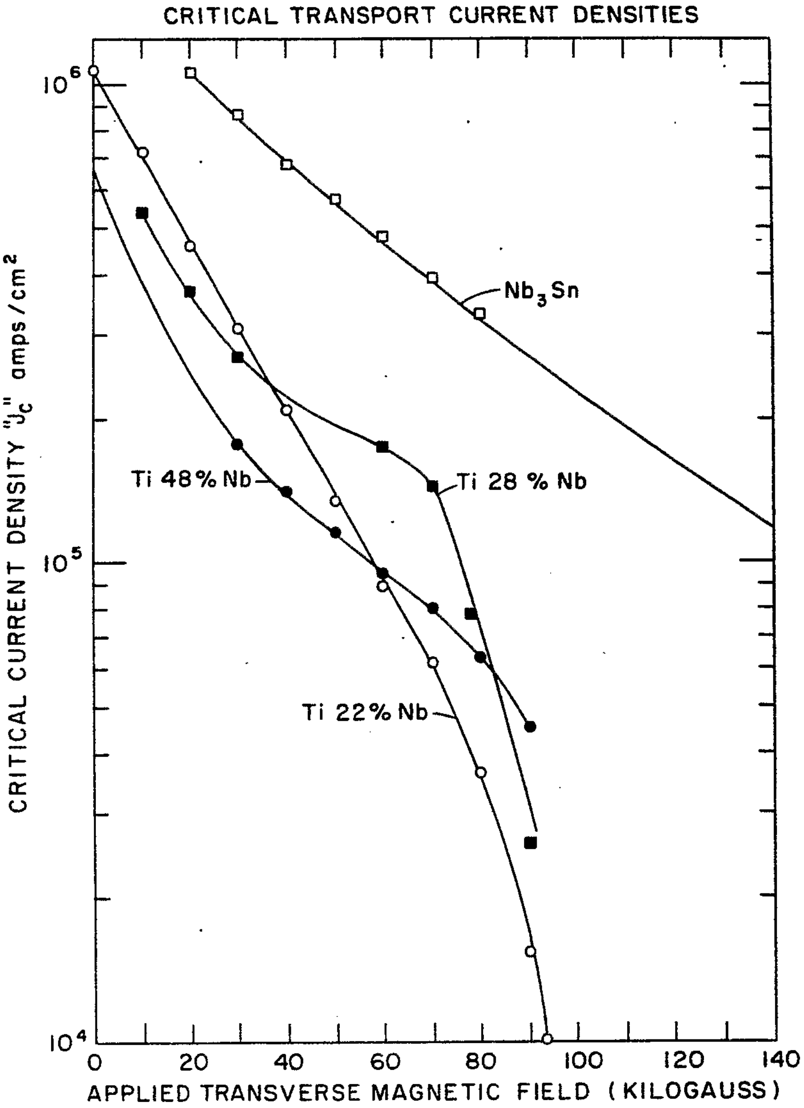

Fig. 8. Critical transport current density vs applied perpendicular field (H) for various type II superconductors.