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SUPERCONDUCTORS BY POWDER METALLURGY TECHNIQUES

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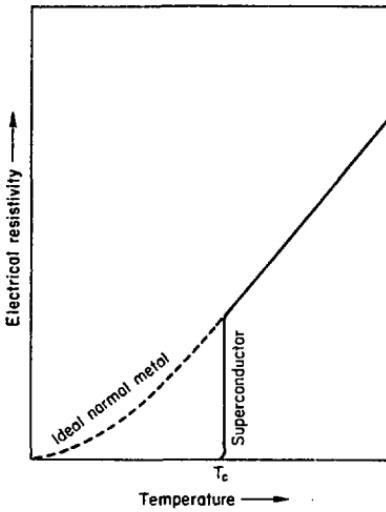
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1. INTRODUCTION AND HISTORICAL BACKGROUND

It had been assumed for a long time that the electrical resistance of metals decreases continuously as the temperature is lowered. Then, in 1911, H. Kamerlingh Onnes,¹ who was the first to liquify helium, made a surprising discovery. While measuring the properties of materials at the low temperatures attainable with liquid helium, he found that at 4.1°K mercury abruptly lost all electrical resistance — it became a perfect conductor. The phenomenon became known as superconductivity. The difference in behavior between a normal metal and a superconductor is shown in Fig. 1. Two years later, Onnes reported that lead becomes superconducting at 7.2°K. He recognized the possibility of using superconducting materials for generating very large magnetic fields with a small expenditure of energy. Immediately, he set about constructing a superconducting solenoid to verify his expectation. The hope was short lived. He found that very small magnetic fields completely destroyed the superconductivity. After the original excitement subsided, research activity on superconducting materials remained at a low level for 50 years.

The dream of Onnes suddenly became a reality as a result of two related discoveries. In 1954, Matthias and his co-workers² reported that the intermetallic compound, Nb_3Sn , becomes superconducting at 18°K, a new record for the transition temperature (T_c) from the normal to the superconducting state. In view of the history of discouraging experiences with superconductors exposed to high magnetic fields, it was not until 1961 that the potential of Nb_3Sn was investigated. That year a break-through was announced by the Bell Telephone Laboratories. J. E. Kunzler et al.³ found that Nb_3Sn could sustain a resistanceless

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Figure 1. Comparison of the behavior of a normal metal and a superconductor.

current density in excess of 100,000 amperes/cm² in magnetic fields up to 88 kgauss (kG), the highest field available to them. It is now known that the critical magnetic field (H_{C2}) of Nb₃Sn is over 200 kG. The magnitude of this field may be appreciated by considering that the earth's magnetic field is about 200,000 times smaller.

These discoveries sparked a tremendous revival of interest in high field superconductivity in laboratories all over the world. Scientists and engineers are presently engaged in three parallel pursuits: (1) a search for superconducting materials with still higher critical temperatures (the latest record of 23°K was established recently for the metastable compound Nb₃Ge^{4,5,6}); (2) the development of viable methods for fabricating superconducting tape and wire based on these compounds; and (3) the application of superconductors in systems with the potential for enormous social benefits. Superconductivity now offers the prospect for electric power generators and transmission lines with capacities many times greater than currently possible; for levitated transit systems capable of jet speeds; and for the only economically feasible way of producing the large magnetic fields required for the confinement of ionized gases in controlled thermonuclear fusion and MHD combustion.

The most widely used superconducting material at the present time is an alloy of niobium and titanium. Although this alloy does not have the high field properties of Nb_3Sn and similar compounds, it has the great virtue of being ductile, and therefore can be fabricated by conventional metal working processes. In contrast, the intermetallic compounds with superior superconducting properties are extremely brittle. Therefore, special procedures must be devised to make them available in the required forms. A number of methods have been developed for Nb_3Sn type compounds in various laboratories. Our laboratory has concentrated its efforts, over the past several years, on the unique capabilities of the powder metallurgy approach. In the following discussion of the different types of fabrication techniques that have been employed over the past 15 years, it will be seen that the use of powder metallurgy has come full circle. It was the first process to yield a practical high field superconductor; was later abandoned in favor of other methods; and now once again appears to be a viable contender.

Although there are known superconducting compounds that have higher transition temperatures than Nb_3Sn ($T_c = 18^{\circ}K$), such as $Nb_3(Al,Ge)$ ($T_c = 21^{\circ}K$), and Nb_3Ge ($T_c = 23^{\circ}K$), practical methods for producing wire or tape have been developed only for Nb_3Sn . The other two compounds mentioned still remain a challenge. The critical temperature and field of a number of high field superconductors are shown in Table I.

Table I. High Field Superconductive Compounds (Niobium Based)

Compound	T_c ($^{\circ}K$)	H_{C_2} at $4.2^{\circ}K$ (kG)
Nb_3Ge	23	380
$Nb_3(Al,Ge)$	21	400
Nb_3Ga	20	200
Nb_3Al	19	300
Nb_3Sn	18	230
$NbTi$	10	120

It is not the intent of this report to discuss, or even cite, all of the processes that have been developed or proposed for niobium-tin superconductors. Rather, the discussion will be restricted to a selected few that will serve to indicate the chronological progress

that has been made. Also, these processes will provide a reference frame for assessing the merits of the powder approach.

2. THE BELL TELEPHONE PROCESS

The first practical process for producing a high field superconductor was developed by J. E. Kunzler et al.³ using a powder metallurgy approach and refined by K. M. Olsen et al.⁷ Elemental powders of niobium and tin were intimately mixed and packed into a niobium tube. An outer jacket of monel was used to cover the niobium tube in order to facilitate wire drawing. This composite could be mechanically reduced to fine wire with a diameter as small as 0.2 mm. At this stage the wire, containing a ductile core of the unreacted powders, could be wound easily to form solenoids. The latter were then heated for several hours at 950-1000°C. During this heat treatment the niobium and tin reacted to form a core of the brittle compound, Nb_3Sn . Many superconducting magnets constructed with this wire have operated successfully. The necessity of winding the coils before carrying out the diffusion reactor was a serious drawback that eventually led to the abandonment of the "wind and react" technique. The importance of the process must not be overlooked, however, because it established the feasibility of high field superconducting magnets and provided the stimulus for a greatly expanded research effort by many laboratories.

3. THE GENERAL ELECTRIC TAPE PROCESS

In order to avoid the necessity of heat treating the entire solenoid, research at the General Electric Research and Development Center was oriented toward the development of a superconductor that could be wound after the reaction to form Nb_3Sn was completed. This requirement implied a configuration in which the superconducting compound was present as a thin layer. In 1966 M. G. Benz,⁸ utilizing the knowledge generated in prior work⁹ at the General Electric Laboratory, described a procedure for fabricating a flexible tape which, with modifications and improvements, is still being produced on a commercial scale.

In essence, a niobium tape is passed through a molten tin bath and then heated in the temperature range 950-1000°C to produce by a diffusion reaction an approximately 2 μm thick surface layer of the Nb_3Sn compound. This tape is then built up as a laminated composite to provide reliable performance. First a layer of copper is applied to each side. The copper is necessary for 'stability', a requirement of such importance that it will be discussed in some detail in the next section. An additional layer of stainless steel may be applied when high strength is required. An important feature of this laminated configuration is the fact that the brittle Nb_3Sn layer is close to the neutral axis of bending. As a consequence, the flexibility is not

diminished by the application of the additional layers. Laminated conductors of this type were used as far back as 1966 to construct a superconducting magnet with a 1-inch bore capable of generating a magnetic field of 100 kG. Despite the many successful applications of this laminated conductor, it has an inherent limitation that has led to the development of more sophisticated conductor configurations.

4. THE QUESTION OF STABILITY

In advanced technologies, a demand has developed for magnets with larger bore sizes and the capability of operating reliably at higher fields. When efforts were made to satisfy these demands 'instabilities' causing magnet damage became a serious problem. The stability of superconductors will be discussed briefly at this point, since it has an important bearing on conductor design.

A high field superconductor is characterized by three basic parameters: the upper critical field (H_{c2}), the critical current density (J_c), and the critical temperature (T_c). The values of these parameters determine a critical surface above which the material behaves in a normal, resistive manner and below which the material is superconducting. This situation is illustrated schematically in Fig. 2 which shows a section of this surface on the applied magnetic field (H) — operating temperature (T) plane.

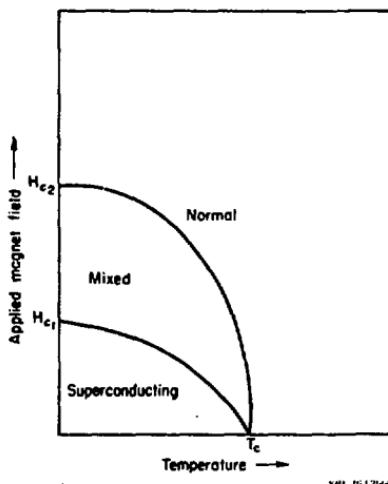
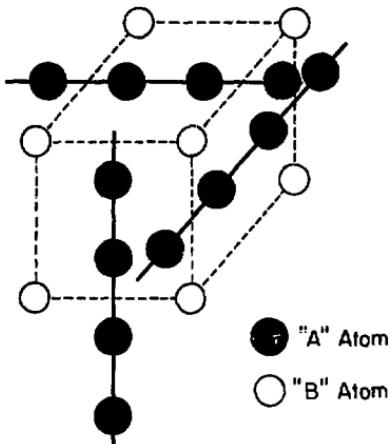


Figure 2. Behavior of a high field superconductor as a function of applied field and temperature.

A fundamental feature of high field superconductors is the gradual penetration of magnetic flux as the field increases beyond a certain value H_{C1} , called the lower critical field. Any small perturbation in conditions (e.g., thermal, magnetic, or mechanical), when $H_{C2} > H > H_{C1}$, can cause a small change in penetration depth, known as a flux jump. A flux jump generates a small amount of heat. The jump occurs so rapidly and the diffusivity of heat is so low that a small localized rise in temperature takes place. Under certain conditions the effect can be cumulative — one jump inducing another in a chain like reaction — and the resulting temperature rise can lead to a catastrophic destruction of superconductivity. The tendency for flux jumping to occur is called 'instability' of performance. The objective of 'stabilization' in advanced conductors is to control flux jumping so that the effects remain within safe, acceptable limits.

In the example of the General Electric tape a degree of stability is achieved by bonding the superconducting compound to a normal metal with high thermal and electrical conductivity, that is in close contact with the liquid helium bath. The normal metal provides an electrical shunt and heat sink to dissipate the effect of a flux jump. This method, called cryostatic stabilization, is limited in two respects: it requires a large ratio of normal metal to superconductor, thus reducing the current carrying capacity of the conductor, and complicates equipment design.

An extensive treatment and review of stabilization criteria has been provided by the Rutherford Laboratory Superconducting Applications Group.¹⁰ Of the various criteria discussed, the so called adiabatic criterion is the most basic. For intrinsic stability, it requires that a superconductor should not exceed a certain critical size, that is determined by certain properties of the superconducting material. In view of the adiabatic and other criteria the preferred size is generally considered to be 10 microns or less. The necessity for such small sizes has given superconductor research a new objective: the development of composite conductors consisting of a large number of superconducting filaments arrayed in a normal matrix. As one would expect, multifilamentary conductors were readily achieved with the ductile niobium-titanium alloy, and these have been developed to a high degree of sophistication, involving twisting, braiding and cabling. A not unusual example is a 200 micron diameter wire, with a copper matrix containing more than 1300 niobium-titanium filaments, each having a diameter of about 4 microns. However, as pointed out earlier, niobium-titanium has a critical temperature of 10°K compared with 18°K for Nb_3Sn , and an upper critical field of 120 kG compared with the 230 kG for the niobium-tin compound. Consequently a great deal of current research effort has been devoted to the development of multifilamentary conductors based on the brittle intermetallic compounds of the Nb_3Sn type. These compounds have the AlS crystal structure, the unit cell of which is shown in Fig. 3. A noteworthy feature of this structure is the presence of orthogonal chains of niobium atoms in close contact. The integrity of the chains is believed



Al5 structure
formula type A_3B

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Figure 3. Unit cell of the Al5 structure.

to influence very significantly the superconducting properties of the Al5 compounds. Disruption of the chains by the presence of structural defects (e.g. vacancies), or by tin atoms occupying niobium positions (in the case of Nb3Sn), results in a lowering of both the superconducting transition temperature and the current-carrying capacity. Of the many compounds of this type, successful processes have been developed only for Nb3Sn, V3Ga and V3Si, with critical temperatures of 18, 15 and 17°K respectively. The remainder of this report will be concerned with multifilamentary composites of Al5 compounds, with emphasis on Nb3Sn, and will begin with a description of a process that must be regarded as the most successful of the non-powder approaches.

5. THE BRONZE PROCESS

The name given to this process derives from the use of a dilute copper base alloy matrix either at the beginning or at a late stage in the process. The solute is one of the metals gallium, tin or silicon which is to become a component element of the desired Al5 compound.

Several research groups appear to have arrived at this approach independently at about the same time. It has been reported¹¹ that a study was initiated in England at A.E.R.E., Harwell in 1969, although nothing regarding this work was published at that time. Details of a process for producing a V₃Ga tape, with a sketch indicating how the technique could be adapted for the production of a multiwire composite, was published in 1970 by K. Tachikawa¹² of the National Research Institute for Metals in Japan. A very brief note regarding the preparation of multifilamentary Nb₃Sn wire, with no procedural details, was published in 1971 by A. R. Kaufmann and J. J. Pickett,¹³ working in the United States. Also in 1971, M. Suenaga and W. B. Sampson¹⁴ of the Brookhaven National Laboratory in New York used this solid state diffusion process to prepare multifilamentary V₃Ga wires, in the manner suggested by Tachikawa. A year later Suenaga and Sampson¹⁵ extended the use of the process to multifilamentary Nb₃Sn. Since then the Brookhaven Group have systematically investigated the influence of the process variables, conducted extensive property determinations to characterize the product and examined the possibility of adapting the process to other Al₅ compounds. The fact that multifilamentary niobium-tin superconductors made by the bronze process are now commercially available in the United States is due in large measure to the development work of the Brookhaven Group. They have concluded that the process can be used for a limited number of systems, specifically Nb₃Sn, V₃Ga and V₃Si. The process does not appear to work for Nb₃Ga, Nb₃Al or Nb₃(Al,Ge).

In the original form of the process, an ingot of copper — 10 wt% tin is cast in a cylindrical shape. A number of axial holes are drilled, in which niobium rods are inserted. Using frequent intermediate anneals, because of the tendency of the bronze to work harden rapidly, the composite is mechanically reduced to a convenient size. The resulting product is then cut into short lengths, a number of which are bundled together in an appropriate container, and the new composite is reduced in the same fashion. This sequence is repeated as many times as required to reduce the niobium cores to filamentary size.

After completion of the mechanical reduction, the multifilamentary wire is heated in the temperature range 650–750°C for times up to 120 hours. During this heat treatment tin diffuses from the bronze to the surface of the niobium filaments and forms a layer of Nb₃Sn between the niobium cores and the bronze matrix. The thickness of the Nb₃Sn layers is typically of the order of 2 microns.

In a later modification due to Suenaga and Sampson¹⁵ pure copper is used in place of the bronze matrix. The objective is to take advantage of the ductility of copper to eliminate the necessity for the time consuming intermediate anneals. The procedure is otherwise identical to the original version up to the final stages. The niobium-copper composite wire is passed through a molten tin bath to apply a coating of tin. Then during the heat treatment, the tin diffuses first into the copper to form a bronze, and from the bronze to the niobium

as in the original process.

6. MULTIFILAMENTARY TAPES BY THE POWDER APPROACH

Our first efforts were directed toward the development of a flexible tape that could be wound to form solenoids after all processing operations had been completed. The procedure that evolved from this work and the superconducting properties of the tape have been reported in some detail.^{16,17,18} The main features of the process and the product will be reviewed briefly to indicate why the process was modified to produce the conductor in the form of wire rather than tape.

The sequence of operations used in the powder process for producing tape is shown schematically in Fig. 4.

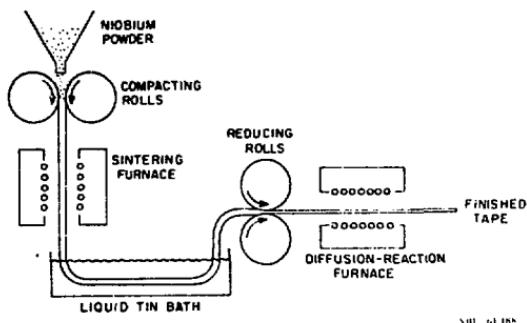


Figure 4. Infiltration process for multifilamentary tape.

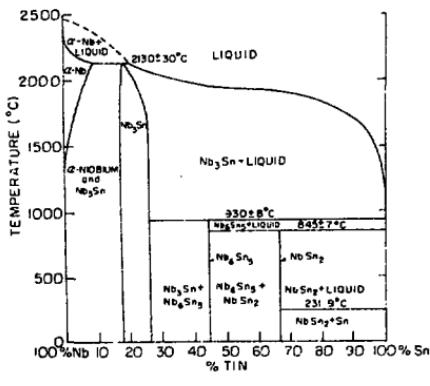
Niobium powder produced by the hydride-dehydride process is gravity fed to a pair of 2 inch diameter compacting rolls. The emerging tape, with a porosity of the order of 30%, can support approximately 800 inches of its own weight. After vacuum sintering for 3 minutes at 2250°C, the tape is quite ductile — it can sustain a bend of 0.1 inch radius. The porosity is moderately reduced to a level of about 25%.

The sintered tape is immersed for one minute in a molten tin bath maintained at a temperature of 850°C to infiltrate the interconnected pore network with tin. While infiltration can be carried out successfully at lower temperatures such as 600-650°C, problems were encountered in the subsequent rolling operation. As a result of the low flow stress of pure tin, some of it was squeezed out during the necessary mechanical deformation, and this tin loss reduced the volume fraction of the superconducting compound, Nb_3Sn , in the final product. The kinetics of

the reaction between niobium and tin are such that after infiltrating at 650°C the only phases present are niobium and pure tin. Raising the infiltration temperature to 850°C resulted in the formation of a significant amount of intermediate phases — predominantly Nb_3Sn_5 . While one might speculate as to the specific mechanism involved, the fact is that the presence of these phases prevented any tin loss during the deformation.

A reaction treatment above 930°C, immediately after infiltration, would produce Nb_3Sn in massive form and the tape would be extremely brittle. By interposing a cold-rolling operation between the infiltration and the diffusion reaction stages, the tin is elongated and thinned to a filamentary morphology, resulting in several benefits. The greatly increased interfacial area between the niobium and tin reduced the time for complete reaction of the tin from more than 20 hours to a few minutes. As pointed out earlier, a filamentary structure is desirable from the standpoint of conductor stability. The filamentary structure also provides the flexibility required for coil winding. A suitable structure was obtained by cold rolling the infiltrated tape to a reduction in thickness of 75-85%.

According to the niobium-tin phase diagram (Fig. 5),



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Figure 5. Niobium-tin phase diagram.

the only phases existing between 930 and 1350°C are niobium, the intermetallic compound Nb_3Sn , and liquid tin. It is in this temperature range, therefore, that the final diffusion-reaction is carried out. However, as mentioned previously, the current-carrying capacity degrades rapidly when reaction temperatures exceed 1000°C, as a result of the thermally induced disorder in the niobium chains of the A15

structure. It is in fact desirable to carry out the reaction at as low a temperature as practicable, balancing the superconducting properties against the required time at temperature. The tapes are normally heated for 3 minutes at 950-975°C. The completed tapes exhibit high values for important superconducting parameters: a critical temperature of 18.1°K, and an overall current-carrying capacity, at 4.2°K, close to 100,000 amps/cm² in an applied field of 100 kG. There is, however, a less than optimum filament morphology in the tapes. The filaments have a typical cross section of 30 microns in width and 5 microns in thickness. According to the stability criteria discussed in section 4, no dimension in a filament section should exceed ~10 microns. In the powder rolling process there is little control over the filament width, which is directly related to the original pore size. For this reason research was undertaken to adapt the process to the production of wire.

7. MULTIFILAMENTARY WIRE BY THE POWDER APPROACH

In modifying the tape procedure, the main features of infiltrating a porous niobium form with tin were retained, since the results were highly satisfactory. The powder rolling step, however, had to be replaced by a more appropriate mode of compaction. In preliminary experiments, two variations of pressureless sintering¹⁹ were tried. First, niobium powder with a particle size range of -325 + 400 mesh was packed into niobium tubes and sintered for 10 minutes at 2250°C. Several difficulties were encountered. Both the size and the volume fraction of the pores were so large that it was not possible to obtain a suitably fine filamentary structure. Also the shrinkage was not uniform and circumferential cracks were observed adjacent to the niobium inner wall. A two stage pressureless sintering was then investigated, using a wider range of particle sizes that included all that passed through a 400 mesh screen. A preliminary sintering of the loose powder in a mullite tube at ~1600°C resulted in a self-supporting niobium rod. After removal of the mullite tube, a final sintering for 10 minutes at 2250°C yielded an acceptable product. However, the necessity for two sintering operations was considered to be too inconvenient, and pressureless sintering was abandoned in favor of isostatic compaction.

The process, as used currently, is shown schematically in Fig. 6. Niobium powder with a sieve range between -250 and 400 mesh is cold isostatically compacted at a pressure of 30,000 psi to give a rod form. After vacuum sintering for 12 minutes at 2250°C the rods are infiltrated with tin by immersion in a tin bath at 750°C for 30 seconds. A photomicrograph of the infiltrated structure is shown on the left in Fig. 6. The white areas, indicating the original pore structure, are tin. The matrix is unalloyed niobium. Since it is difficult to wire draw niobium because of its tendency to gall, and since the tin must be prevented from being squeezed out, a double cladding is employed. The inner jacket is niobium which serves to retain the tin and prevent undesired diffusion reactions between the infiltrated core and the outer

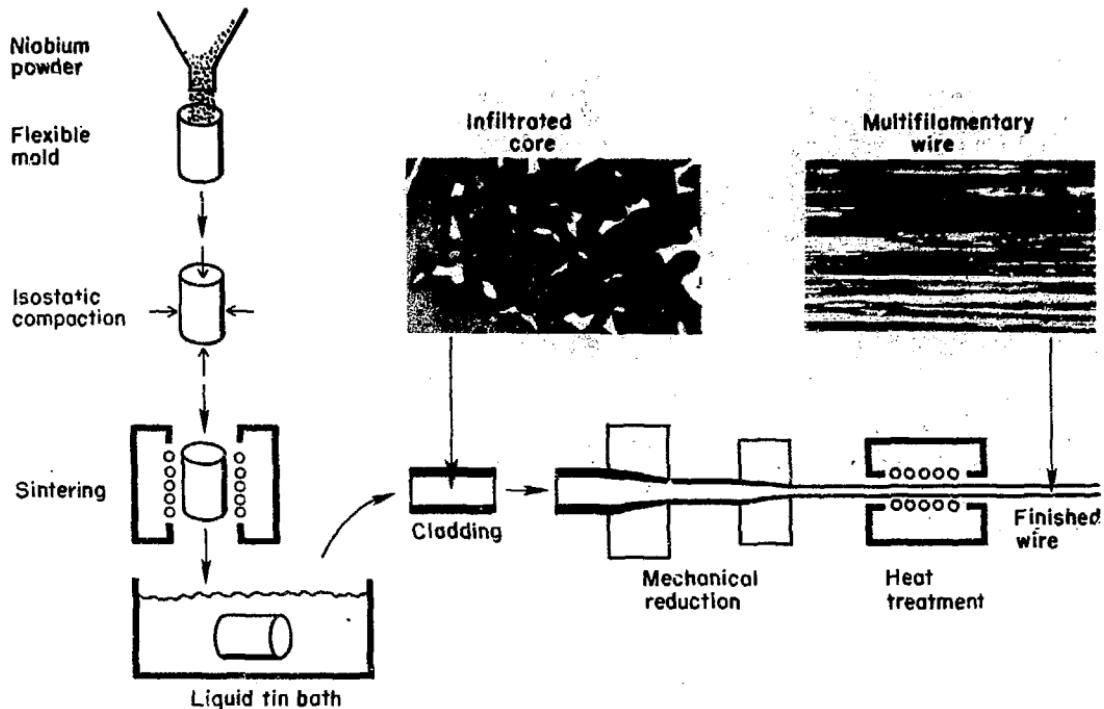


Figure 6 - The infiltration process for producing multifilamentary superconducting wire.

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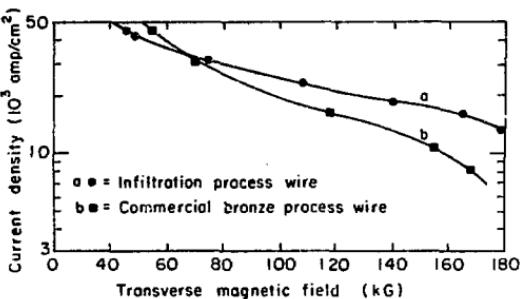
jacket, which is usually monel or copper tubing. Either of the latter greatly facilitates wire drawing.

The composite rods are reduced to wire with diameters in the range of 10 to 15 mils, usually by form rolling followed by wire drawing. A heat treatment for 2 minutes at 950°C is sufficient to cause all of the tin to react with the niobium matrix to form filaments of the superconducting Nb_3Sn compound. These filaments are well within the desired size range, having transverse dimensions of the order of 1 to 2 microns. A photomicrograph of a longitudinal section of the finished wire is shown on the right in Fig. 6. The light areas are the niobium matrix and the dark filaments are Nb_3Sn .

8. CURRENT ASSESSMENT OF P/M SUPERCONDUCTING WIRE

The bronze process, which was described in section 5, is widely regarded as representing the present level of niobium-tin technology. As mentioned, this process has been intensively studied and optimized by the collective efforts of many research groups. In contrast, the new P/M wire has not yet been optimized. For example, it is well known that the current-carrying capacity of niobium-tin conductors can be substantially enhanced by doping with zirconium. The magnitude of the effect of doping on the P/M wire remains to be determined. Nevertheless, it is interesting to compare the superconducting properties of wires made by the two processes and tested under identical pulsed field conditions.

The overall critical current density as a function of transverse magnetic field is shown in Fig. 7 for representative wires.



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Figure 7. Overall critical current density vs applied field for infiltration process and bronze process Nb_3Sn wire.

Curve a was obtained for the P/M wire, and curve b for the bronze process wire.

The P/M wire with its cladding has a diameter of 0.013". It is a single core wire with a core diameter of 0.009". The size of the Nb₃Sn filaments is between 1 and 2 microns. The wire which has a critical temperature of 18.1°K was reacted for 1 minute at 930°C.

The bronze-process wire, which has a diameter of 0.012" and contains more than 1000 niobium-1% zirconium cores, was made by repetitive wire bundling and mechanical deformation. It required a reaction time of 70 hours at 700°C. The Nb₃Sn layer thickness around each core is 2 microns.

Bend tests performed on both wires indicate that the P/M wire suffers less degradation of current-carrying capacity for a given diameter bend. The bronze process wire showed a 20% degradation after a 2.5 cm bend. To produce the same degradation, the P/M wire had to be bent to a diameter of 1.5 cm.

The results on the niobium-tin system are quite encouraging. The P/M wire already appears to have superior high field properties. Work is in progress on other Al₅ compounds. The P/M approach will take on added significance if it can be shown that it is equally applicable to some of these compounds for which the bronze or other alternative processes are not viable.

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