NB BASED SUPERCONDUCTOR COMPOSITES

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Introduction

The technology for the manufacture of composite superconductor material is well established. An excellent paper (1) covering the technology of superconducting composites has been written by H. Hillman for publication in The Proceedings of NATO Advanced Study Institute on Superconducting Materials Science and Technology. In this paper, I will address the relative manufacturing merits of several different composite approaches, including filled billet, powder, in-situ casting, and rolled sheet methods.

Each method has common goals: (1) fine filaments with 1 micron to 10 micron dimensions; (2) continuous filaments; (3) cryogenic stabilization capability; (4) electrical stabilization capability; (5) long lengths, 2000 meters or more; (6) strain tolerance (for A-15 conductors); (7) design versatility; (8) diffusion barriers for A-15 conductors; (9) economy. Most methods are able to meet several of the desired characteristics, but fall short in several other characteristics. One method, a modification of the rolled sheet method, has been shown to meet all the required characteristics.

Filled Billet Construction Methods

The filled billet method includes several variations:

1. Drill longitudinal holes in a billet of matrix metal (Cu, bronze, etc.) and fill the holes with rods of the superconductor component (Nb, NbTi, V, etc.).

2. Insert rods of the superconductor component into tubes with a round inside diameter and a hexagonal outer shape, and bundle these together into a container.

3. Insert a rod of matrix metal into a tube of superconductor metal, rebundle into hexagonal matrix tubes, and bundle in a container. After a billet has been constructed, fabrication proceeds in the usual fashion of extrusion and drawing to produce wire (details can be obtained from Hillman's paper (1)).

The first approach, drilled and filled billets, requires machining to maintain close diameter and alignment tolerances for the holes. High current density in a conductor requires that a high percentage of the cross section be superconductor. Drilled holes become more difficult to make within close tolerances when the hole is long and the diameter is small, both conditions which are desirable for economy of fabrication. The requirement for filament diameters of 1 micron to 10 microns in the conductor means that a rod large enough to facilitate billet construction, 0.7 cm ϕ minimum, will require an area reduction of 400,000 to 1 for 10 micron filaments, and 40,000,000 to 1 for 1 micron filaments. Although the method presents difficulties, it is useful for the manufacture of small conductors for technical evaluation purposes. The filaments are continuous and laboratory buttons of superconductor material can be utilized.

An improvement over the drilled billet approach was to utilize hexagonal tubes of matrix metal with round inside diameters. The hexagonal tubes provide good tolerance control for rod insertion, uniform spacing, the versatility to mix electrical stabilizers and strengthening components, and long lengths for material yield improvements. The advantages have been so great that this method has been utilized for the vast majority of all commercial conductor manufacturing to date. However, the difficulties imposed on fabrication to produce a 1 micron to 10 micron filament diameter are not alleviated by this method. The 0.7 cm ϕ rod of superconductor needs to be reduced 400,000 to 1 to produce a filament of 10 micron diameter. Although industry readily produces conductor with 10 micron filaments, economy of manufacture is compromised. Both NbTi and Nb_3Sn conductor is produced with this method.

Another variation of the filled billet method is to utilize thin wall tubes of superconductor material to produce Nb_3Sn conductor. One of the benefits promised is that by starting with thin dimensions, area reduction requirements are significantly diminished. In addition, matrix material can be varied at the inside of the tube from the outside of the tube, utilizing the tube wall of the superconductor as the barrier between dissimilar matrix materials. The two disadvantages of this tube method are that (1) the area of superconductor is limited and (2) tubes of superconductor material are expensive and difficult to obtain.

Powder and In-Situ Methods

The proximity effect describes the observation that superconductivity can pass through normal material when the spacing is sufficiently small. This discovery gave promise for the manufacture of a conductor which has ultra fine but discontinuous filaments. Two methods have received extensive expirimentation. One is the immediately obvious approach of blending elemental powders and processing by normal methods. Mixing Nb and copper powders provides few difficulties for processing. Although the method appears to be interesting at first thought, difficulties become significant for the manufacture of a successful conductor with A-I5 or NbTi filiments.

In order to be sufficiently soft for co-reduction with a ductile matrix, the superconductor component must be of high purity, containing less than 150 ppm oxygen. The generation of Nb powder with low oxygen requires special techniques or special screening of the large particles over 600 micron diameter. Both methods rapidly increase the cost and the apparent economy of the powder method is compromised.

The development of economical methods of alleviating the oxygen problem can promise attractive economies of manufacturing for the conductor. The ultra fine filaments which are readily produced from the powder components promise greatly improved resistance to strain.

Some questions remain. One unresolved problem is that the benefit derived from the proximity effect carries with it a resultant large "effective" filament diameter observed in AC loss evaluation. The magnitude of the losses is large enough to discourage acceptance of conductor until the loss situation is clarified. For A-I5 conductors, if the reactant component must be introduced after the conductor is produced, limitations of stabilizing materials and size (less than 0.5 mm conductor diameter) are imposed. If the solid state diffusion approach is utilized (by blending Nb and bronze powders for example), breakage problems develop during processing as the result of the need to anneal the bronze matrix.

There are some ingenious solutions being studied to resolve the fabrication problems. Success at the studies may enable the production of useful conductor by the powder process. At this time, the degree of processing refinement required to effect the solutions economically appears to be beyond the scope of normal commercial manfacturing. If we are positive in our hopes to find simple and commercial answers to the problems for effective processing parameters in the powder method, one plaguing doubt always remains. Mixtures of powder will always contain the cross section unit which limits the capacity for carrying current. The only reliable method for quality control is to test each entire length of conductor. The cross section which contains the least amount of powder will determine the maximum current capacity. The reliability question can be alleviated by bundling several powder components. The bundling solution increases costs and still provides a conductor with large "effective" filament diameters (i.e. large losses in changing magnetic fields). While the powder method seems promising, the required solutions have remained elusive and are not yet demonstrated commercially.

The widespread interest in the powder approach was stimulated by Dr. C. T. Tsuei's (2) report in 1973 that Nb and copper could be melted and quenched to yield fine precipitates of Nb. Subsequent processing proceeded well because the material demonstrated excellent fabricability, similar to pure copper. Wire produced from the quenched casting demonstrated superconducting characteristics as if the precipitates were continuous filaments. As with powder mixtures, the excitement stemmed from the promise of greatly simplified processing, thereby reducing costs of the conductor. Although much investigative work has been performed with the in-situ casting method, the difficulties of scale up and uniformity problems, which are similar to the powder method, are not resolved. If an application would develop with sufficient volume, minimal electrical and cryogenic stabilization requirements, and no AC loss requirements, commercialization of a continuous casting in-situ conductor or a powder method conductor may be realized. Until then, commercialization of the two methods remains to be demonstrated.

Another interesting powder approach is to compact and sinter Nb powder into a porous bar. The particles sinter together to form a continuous network throughout. The bar is then infiltrated with a liquid reactant such as tin. The infiltrated bar can then be cold processed to produce wire. Conductor produced by this infiltration method has a network of ultra fine filaments which are continuous from end to end. The ultra fine Nb filaments enable reaction parameters which can produce very high current densities in a wire cross section.

The infiltration method is limited in application much the same as the other powder methods. Cryogenic stabilization with the present methods can only be accomplished by braiding or cabling copper jacketed wires. The filaments have no possibility for either cryogenic or electrical stabilization, so AC losses and current sharing will always be a major concern for the infiltrated conductor. Alternate processing methods from cold drawing are limited by the low melting infiltrant. Rebundling processes must be cold, so bonding of the clad component is not reliably accomplished. Control of the porosity and sintered grain size through any cross section is difficult, so each wire must be defined by the lowest current carrying region (in the same consideration for powder and in-situ methods), and the lowest region cannot be accurately defined by any test short of full conductor testing. Costs for generating controlled Nb powder, sintering, and infiltrating on a controlled basis for commercialization have not been established. Reduction ratios appear to be limited by the degree of work hardening the sintered filaments can tolerate before local filament fracture occurs, but area reductions of several thousand to one appear possible. As with the other methods, the infiltration method has limits, but where a need for direct current with high current density exists, cost is less important than current density, magnetization losses are less important than current density, and magnetization losses are not important, the infiltration method may provide a useful conductor.

A new powder method for producing Nb_3Sn conductor by starting with $NbSn_2$ powder has been developed in The Netherlands (3). This process can produce high current densities by incorporation of the high tin density available from the $NbSn_2$ compound. The benefits are similar to those of the infiltration method, that is high current density, and processing without anneals. The $NbSn_2$ powder method is accomplished by placing compacted $NbSn_2$ powder into a Nb tube, following the filled billet method, and processing to wire. As with the infiltration method, cold drawing single strands or bundled strands can be accomplished to produce wire. The $NbSn_2$ powder method may have a benefit the infiltration method lacks because of the higher melting temperature (850°C) of $NbSn_2$ than tin (230°C). This higher temperature allows the possibility of extrusion for the $NbSn_2$ method. Although the question of rupture of the Nb tube wall during reduction has not been resolved, the possibility for extrusion is a commercial advantage for the $NbSn_2$

method over the infiltration method. The question of cost for the Nb tube and $NbSn_2$ powder components still remains a problem. Considerable work is progressing in The Netherlands to produce a commercially acceptable conductor by the $NbSn_2$ powder method. If the questions of cost and commercial scale up can be resolved, the $NbSn_2$ powder method can compete with infiltration for the high current density conductor, and has enough versatility in the manufacture for stabilization.

Layered and Rolled Sheet Method

A simple method to produce composites is to layer sheets of the materials together. These layered sheets can be rolled into a cylindrical shape, inserted into a container and processed in the normal manner. No processing limitations beyond any other method exist for the rolled sheet method. Advantages for processing are quickly seen as obvious because of versatility in component dimensions. Where thicknesses of superconductor are preferred to be on the order of 1 micron, the superconductor starting thickness can be tailored to the area reduction ratio planned for the billet. Electrical and cryogenic stabilizers can be incorporated, and diffusion barriers to protect the high purity stabilizer can be included. Small billets for evaluation can be constructed which will represent the product of a full scale conductor. However, the problem of eddy current loops forming on expansive, continuous superconducting surfaces is severe. Rolled sheet composites cannot be sufficiently reduced to eliminate the excessively large superconducting surface perpendicular to current flow. Associated problems, such as magnetization losses, flux jumping, and the associated heat generation, produce a generally unacceptable conductor.

Eliminating the expansive surface of superconductor which is perpendicular to current flow is the easiest way to utilize all the advantages of the rolled sheet method while simultaneously eliminating the intolerable problem. This solution is readily achieved by introducing a discontinuous or foraminus layer of superconductor. The superconductor sheet is slit into strands which are about 1 1/2 times wider than thick. The material being studied at TWCA (4) utilizes expanded metal sheet, commonly produced in industry. The superconductor strands are regularly connected at one or two centimeter intervals in the starting material. Processing the layered billet into wire extends the connection 10,000 to *40,000* times (equivalent to the applied area reduction). Any losses which may result because of the filament connections are readily controlled by twisting the wire, the twist pitch being much **less** than the distance between connecting filaments.

All of the goals desired for conductor are'met with the TWCA layered foraminous sheet method. Coils of conductor with fine filaments (approximately 1/2 micron) have been produced in continuous coils of 3700 meters to *4000* meters at 0.32 mm ϕ. The filaments are continuous and spaced by the matrix bronze sheet so the filament spacing is controlled. Copper for stabilization has been included at the center or outside or both, in the desired amounts from 20% by volume to 85% by volume. The fine filaments are produced from 7.6 cm ϕ billets with no bundling or double extrusions required. The fine filaments enable the formation of fine grain Nb_3Sn for optimized current densities, and for improvements in strain resistance approaching that of in-situ and powder conductors while maintaining continuous filaments, low losses, and stabilization. As in other methods which produce fine filaments, inherent strength in the conductor is benefitted. The ease of billet construction allows design versatility including variation of Nb_3Sn filament dimensions within the conductor, inclusion of components for strength benefits, diffusion barriers, and filament spacing. Probably the most significant aspect of the layered foraminous sheet method is the large reduction in cost while maintaining all the benefits of conductor produced by other methods.

Summary

The manufacture of superconductor composites has taken several forms. The goals are much the same, primarily:

1. Finest possible filaments, 1/2 micron to 1 micron optimum.
2. Continuous filamentary network.
3. Capacity for stabilization and protection.
4. Long lengths suitable for large scale hardware.
5. Strain tolerance (for A-15 conductors).
6. Versatility of design to diffusion barriers and strengtheners.
7. Economy of manufacture.

The goals met by each method discussed are summarized:

A. Filled Billet:
   1. Costly and extreme reductions required to achieve 1 micron filaments.
   2. Excellent continuous filamentary network.
   3. Excellent stabilization and protection capacity.
   4. Excellent capacity for very long, useful lengths.
   5. Moderate to poor strain tolerances because of difficulty to achieve 1 micron filaments.
   6. Excellent design versatility.
   7. Expensive to manufacture (for A-15); good economy for NbTi conductor.

B. Powder and In-Situ:
   1. Economical manufacturing methods expected, but quality control and reliability must be domonstrated and can be expensive.
   2. Filaments are continuous but interconnected with resultant unacceptably large magnetization losses in changing magnetic fields (AC losses).
   3. Difficult to stabilize except by bundling.

4. Excellent lengths possible.

5. Excellent strain tolerance results from ultra-fine filamentary network.

6. Limited versatility of design because of the need for particle mixtures.

7. A promise of economy exists, but has yet to be domonstrated.

$NbSn_2$ Powder Method:

1. Fine filaments and large area of superconductor possible, but reduction ratios must be large (400,000 to 1 or greater) and therefore expensive.

2. Excellent continuous filamentary network.

3. Excellent stabilization and protection capability.

4. Breakage due to tube wall rupture has yet to be resolved for long length manufacture.

5. Moderate strain tolerances exist as is expected until ultra fine filaments are achieved, and that capability seems unreasonable for this method.

6. Excellent design versatility similar to filled billet methods.

7. Expensive materials and controls limit the promise of economy for this method.

C. Layered and Rolled Foraminous Sheet Method:

1. Excellent economy for fine filament manufacture, resulting from the small dimensions of the foraminous sheet.

2. Excellent continuous filamentary network, with filament connection instabilities controlled easily by twisting, a normal requirement for all multifilamentary conductors.

3. Excellent stabilization and protection capacity.

4. Excellent capacity for very long, useful lengths.

5. Improved strain tolerance resulting from fine filaments.

6. Excellent design versatility.

7. Outstanding economy of manufacture in comparison to the other manufacturing methods useful for practical conductor.

References

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