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FABRICATION OF SUPERCONDUCTING WIRES

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SUMMARY

In this paper the established wire production route for superconducting applications is reviewed. The alterations to the process are also briefly touched upon.

SÜPERİLETKEN TELLERİN YAPILMASI

ÖZET

Bu derleme makalede, süperiletkenliğin uygulamalarında kullanılan en yaygın ve oturmuş çok-filementli tel üretme metodu gözden geçirilmiş ve metoda yapılan değişikliklere de kısaca değinilmiştir.

1- INTRODUCTION

When H.K. Onnes [1] found the vanishing of the resistivity of Hg at very low temperatures in 1911, the technological potential of such a property (state) was evident, although existing theory was unable to explain the phenomenon. But material and cryogenic pratice had to be established for technological applications.

A few decades of search, both in pratice and theory, brought the ductile metals and metal alloys into use for superconducting applications. This was for magnetic inductions up to about 7-8 Tesla applications with Nb-Ti ductile alloy superconductors. Early magnets built from this ductile alloy were notorious for instabilities or "flux jumps" which severely limited their performance. In 1960 two techniques were developed to evercome this problem. One is mainly adding enough copper to the superconductor so that if all the current was carried by copper the joule heat could be carried away by boiling helium while the temperature of the conductor remained very close to the bath temperature, and is called cryostabilizing [2,3] . The other was dividing the superconductor into fine filaments in a normal matrix and twisting them [4,7] . In the latter case it was shown that the magnetic energy available for the flux jumps was ruduced greatly, ant stable magnets could easily be built. These two developments contributed greatly to the present state of applied superconductivity.

While technology was advancing to make full use of ductile Nb-Ti and Nb-Zr alloys, the search was going on to discover new superconductors with better properties than those of existing ones.

1.1- Discovery of superconductivity in A15 compounds and Nb_3Sn

The search was intensive in Bell Laboratories in 1950's for better superconductors. They discovered a couple of dozen new superconductors. But it was the discovery of superconductivity in silicades and germanades which intensified the work even harder. In 1953 Hardy and Hulm [8] reported superconductivity (Superconducting transition temperature, T_c = 17K)in V_3Si as superconducting A15 material with six other silicades and germanades.

In 1954 Matthias et al [9] reported superconductivity in Nb_3Sn (17.5-18.5K; 5.3Å) and Ta_3Sn. Finally Kunzler et al. [10] reported critical current density of 10^5 A/cm^2 at 8T in Nb_3Sn. This last result started a new era in applied superconductivity.

Following this, several Nb_3Sn tapes, then magnets were produced. Kelbe et al. [11] produced cryostrand Nb_3Sn wires by liquid diffusion; Martin et al. [12] built the first 10T Nb_3Sn tape magnet by liquid diffusion in 1963; Hanak et al. [13] employed chemical vapour deposition to produce Nb_3Sn tapes; Fietz et al. [14] used plasma spraying of Nb and Sn powders onto substrates and formed winding by selective masking, and several others [15,16] .

But ductile niobium alloys still enjoyed superiority because of easy fabrication into wire form and other reasons. Real activity and hope for use of Nb_3Sn for large scale applications started with the discovery of the "bronze process" which made Nb_3Sn available in wire form.

2- DISCOVERY OF THE "BRONZE PROCESS"

The effect of Cu, in enhancing the growth of V_3Ga at the expense of other Ga rich nonsuperconducting compounds was known as early as 1967 [17] . Actually Tachikawa et al. found that it did not only enhance the A15 growth but made the A15 layer uniform as well in their tapes. But actual "bronze process" was discovered in three different countries at about the same time. Tachikawa [18] in Japan, Kaufman and Pickett [19] in USA and Howlet [20,21] in UK separately discovered the process in 1969-70. Tachikawa reduced V in Cu,Ga matrix to tape form and later formed V_3Ga by solid state diffusion. The others reduced Nb-(Cu -Sn) composite to wire form and later formed Nb_3Sn by a solid state diffusion process.

The "bronze process" is, briefly, reducing Nb (V) in a Cu-Sn (Cu-Ga) matrix, and drawing it to the final form and size required and deferring the heat treatment to form the A15 compound until the end. Full description of the process will be given in section 4.

3- MODIFICATIONS TO THE "BRONZE PROCESS"

3.1- Diffusion barrier

Since there is always some residual tin in the matrix of abronze processed superconductor even after full reaction, one has to provide separately the high conductivity path for stability. This high conductivity element has to be protected from tin contamination during diffusion heat treatments.

The idea came from the Harwell group [22] to incorporate high purity copper into the composite, protected from tin contamination first by a Ta barrier [23,24] and later by phosphorus poisoned Nb [25] . The latter reducing the number of materials incorporated into the composite which simplifies the drawing processes and reduces the overall cost of the product.

3.2- External diffusion

The bronze process has two principal disadvantages; one is the limit set for the superconductor to matrix ratio by the solubility of Sn in Cu, the other is the intermediate annealings necessary to remove the work hardening of Cu-Sn matrix.

Soon after the discovery of bronze process, the external diffusion process was introduced [26,27] to eliminate these disadvantages. Briefly, Nb rods were reduced in a Cu matrix to the final size then tin plated before the final reaction to form Nb_3Sn. This eliminated the intermediate annealings necessitated by the bronze matrix and the limit set by the Sn solubility (9.1 at % Sn) [28] in Cu.

Disadvantages of this process are the size limit set to the wire diameter by the diffusion length of Sn, and the difficulty of inclusion of high conductivity stabilizers.

3.3- Internal diffusion process

Hashimato et al. [29] reported that they assembled Cu-clad Nb bars together with a Cu-clad Sn-20 at % Cu alloy (or pure Sn rod later) into a copper tube and reduced to final size without any intermediate annealings. This was then reacted to form the A15 phase.

The advantages of this process over the "bronze process" is again the elimination of the intermediate annealings.

Other similar modifications are encasing Cu-Sn alloy rod or Cu-clad Sn rod, $NbSn_2$ powder (ECN technique) in a Cu-clad Nb tube and repacking of several of these units in a Cu tube for cold drawing to the final during subsequent drawings. As seen in Fig. 1 this 37-filament unit is drawn to a hexagonal wire form for packing. Short lengths of this hexagonal unit are packet into a tin bronze tube together with six hexagonal pure Cu rods clad with phosphorus poisoned Nb. Phosphorus poisoned Nb acts as the diffusion barrier to prevent tin from contaminating the Cu stabilizers. Phosphorus forms a niobium phosphide layer during reaction heat treatment around the Nb barrier which stops the formation of Nb_3Sn.

This composite is then further deformed by swaging and drawing to the final filament diameter desired, still needing more intermediate annealing. This packing could be repeated until the desired number and size of filaments is achieved. Then the final wire is twisted as seen in Fig. 2. In this way the formation of brittle Nb_3Sn is deferred until the wire takes its final shape.

4.1- Choice of bronze

In producing Nb filaments in a bronze matrix, althoug the ratio of superconductor to matrix can be varied by altering the number of the Nb rods in the starting ingot, an upper limit is set by amount of tin which can be dissolved in copper as solid solution; this is 9.1 at % Sn [28] . If all this tin can be converted into Nb_3Sn leaving pure copper, the maximum superconductor to normal metal ratio would be 38.7 Vol. %. However there is always some residual Sn left in the matrix after reaction.

If higher tin bronzes e.g. α - solid solution plus second phase precipitates, is used, then on reaction σ -phase precipitates dissolve but, where they are in contact with niobium filaments, reaction is very slow. This coupled with more difficult working, limits their value.

In commercial tin bronzes about 0.2 wt% P is used as deoxidant and to improve fluidity in casting. Phosphorus content in excess of size [21,30,31] .

3.4- Other modifications

3.4.1- "In-situ" process

Tsuei [32,33] , in 1973, proposed the most interesting modification to the bronze process. This process consists of casting a Cu-Nb melt to form a dentritic network of Nb in Cu, and of drawing this to wire. Sn can be added into the melt or plated onto the wire before reaction to form Nb_3Sn. This is now the so called "in-situ" process [34].

3.4.2- Powder route

This route is to extrude well mixed and compacted Nb and Cu powders [35,36] to wire form and to add Sn finally before the diffusion heat treatment.

Both these last two routes produce final products which are less sensitive to the effects of strain (see the recent review by R.Roberge [34] .

The other most recent method which is worth mentioning is melt Spinning of Cu-Nb or Cu-Nb-Sn mixture in the hope that one would have densely distributed fine particles of Nb in Cu or Nb_3Sn in Cu,Sn. This work is being carried out as a joint project involving Departments of Metallurgy and Science of Materials, Physics, and Engineering at Oxford,

4- THE MAIN PRODUCTION ROUTE; "BRONZE PROCESS"

The mechanical formation of the superconductor starts with Nb rods inserted into the holes drilled in the required arrangement (37 holes) in a Cu-7.5 at % Sn bronze ingot. The ingot is then deformed by swaging or extrusion to a rod which is deformed further by wire drawing. The problem here is the work hardening of the bronze matrix. For high tin bronzes annealing temperatures in excess of 400°C are necessary. But one has to adopt annealing temperatures below 600°C, otherwise considerable amount of Nb_3Sn forms around the Nb filaments and then breaks up

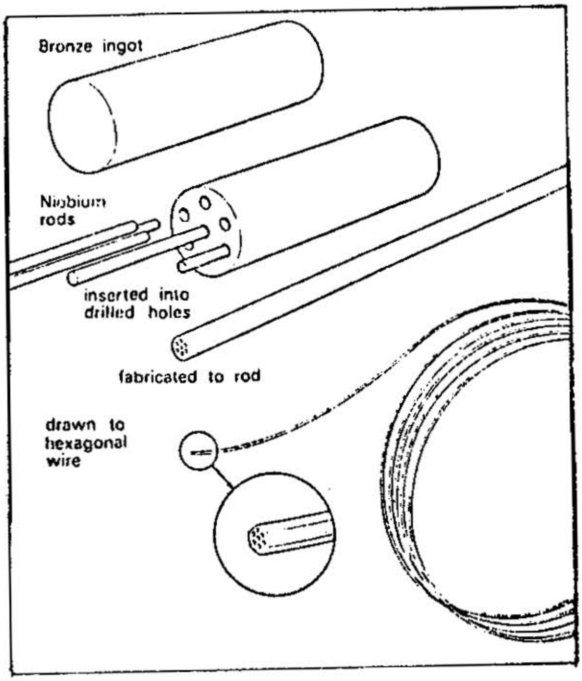

Fig.1- Production route for hexagenal compesite suitable for bundling

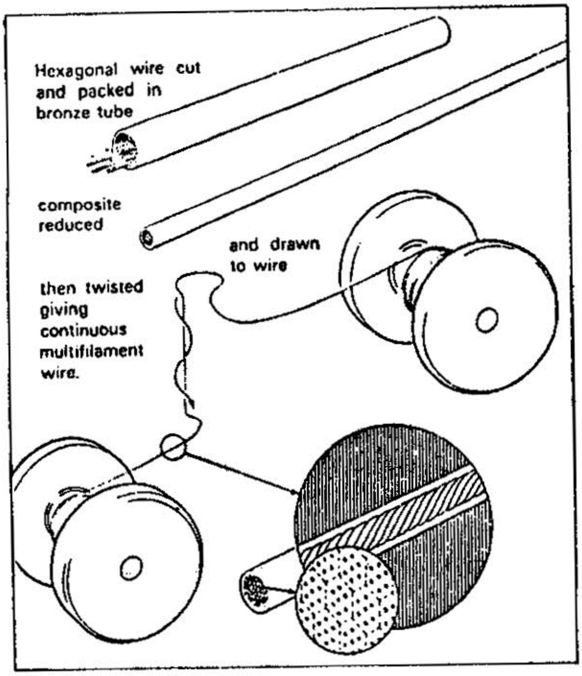

Fig.2- Production route from bundling state to final product [22]

o.o3 wt% [37] slows down the formation of Nb_3Sn to a great extent. Bronze billets with less than 0.02 - 0.03 wt % P vacuum cast from OFHC copper and 99.99 wt% pure tin are used. The ingot is homogenised by machining off the surface, swaging, and annealing before the holes are drilled for niobium insertion.

Phosphorus poisoning is actually achieved by cladding the Nb-clad pure copper with phosphour bronze which is just thick enough to stop the reaction at the Nb barrier but not to reach the neighbouring niobium filaments.

Since the success of the "bronze route" depends on the formation of single phase (A15) layer at the interface of appropriate matrix and the filament material (so called diffusion couple) it is important to consider the thermodynamics involved with the process at this level. Since the thermodynamic considerations and formation of Nb_3Sn by solid state diffusion on its own is a long subject this will be discussed in anather paper.

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