

July 9, 1968

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3,392,055

METHOD OF MAKING SUPERCONDUCTING WIRE

Filed Feb. 1, 1963

Fig. 1.

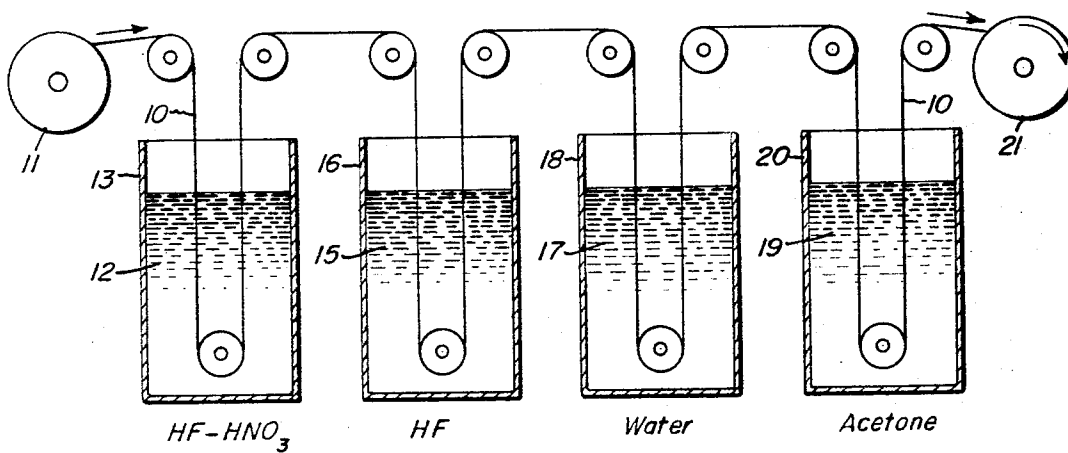


Fig. 2.

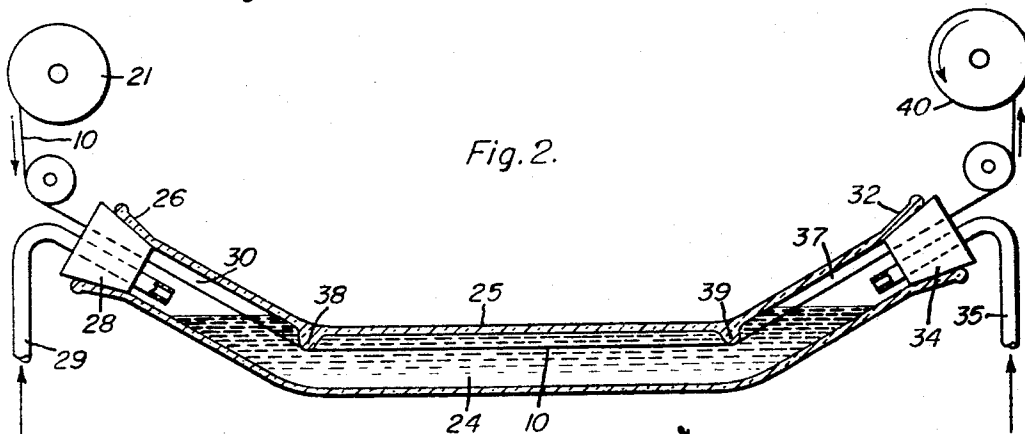
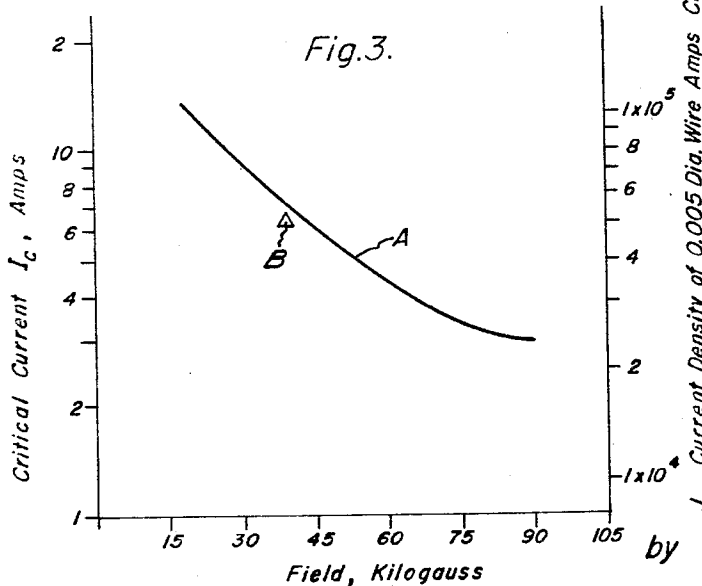


Fig. 3.



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3,392,055
METHOD OF MAKING SUPERCONDUCTING WIRE
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Filed Feb. 1, 1963, Ser. No. 255,474
4 Claims. (Cl. 117—227)

The present invention relates generally to the art of producing superconductors and is more particularly concerned with a novel method of making superconducting wire having high current-carrying capacity and good physical and electrical properties substantially throughout its length.

It has for sometime been generally recognized that niobium-tin compositions in which the ratio of niobium to tin approximates three to one, have superior superconducting properties. Consequently, this alloy has been fabricated in various forms, principally wires, in efforts to produce devices such as high critical field superconducting, electromagnets. In order to overcome working limitations imposed by the brittleness of this material, known generally as Nb_3Sn , others skilled in the art have heretofore resorted to the use of niobium and tin powders, forming the desired shapes in various ways such as by hot pressing. Elongated conductors of wire-like type have been made by filling a hollow tube of niobium with a mixture of tin and niobium powder and drawing or swaging down the tube to produce a composite wire of the desired diameter. While these procedures have proven satisfactory in some respects, they involve shortcomings which have resisted prior efforts to remove them. For one thing, the powder core approach does not lend itself to rapid and economical wire production because of the difficulty of process control to the extent required to produce uniform electrical and physical properties throughout the length of a wire.

The novel concept set forth in the copending patent application of Warren De Sorbo, Ser. No. 149,590, filed Nov. 2, 1961, and assigned to the assignee hereof, of providing a tin coating on a niobium wire either by vapor deposition or by immersion of the wire in a body of molten tin, avoids the shortcomings of powder procedures. Thus, by providing the tin requirement in the form of an envelope or sheath bonded to a niobium wire while eliminating the need for metal-powder working, the problem of producing Nb_3Sn wire has been solved.

According to the present invention, this De Sorbo process is carried out in a continuous manner with the result that long lengths of high quality superconducting wire are obtained consistently. The discoveries underlying this invention and thus enabling this important new result include the fact that when a niobium or niobium alloy substrate wire is properly prepared, only a comparatively short period of contact of such a wire with tin melt is necessary to provide an adequate coating of tin and to establish an essential intermediate layer of Nb_3Sn completely covering the substrate wire. Moreover, we have found that the current-carrying capacity and other desirable properties of such a product can be materially improved or enhanced by prolonged heat treatment conducted under circumstances resulting in growth or thickening of the Nb_3Sn intermediate layer. Another of these discoveries is that unless such a tin-coated niobium or niobium alloy wire is cooled in a neutral atmosphere (i.e. an atmosphere substantially free from gaseous oxygen and nitrogen) to freeze the adhering tin, the resulting product generally will be inferior and not suitable for such purposes as the production of superconducting magnets. We have also found that there is a relatively wide

latitude of choice as to tin dipping bath temperature and period of niobium or niobium alloy wire immersion in the tin dipping which will give consistently good results in terms of the properties of the superconducting wire product. Additionally, we believe that baths or melts of aluminum, gold and gallium may be substituted individually for the tin bath in the present new method and that vanadium wire may be treated with gallium in accordance with this invention to produce long lengths of superconducting wires of superconducting magnet quality. As those skilled in the art will understand, however, such substitutions will in some instances impose special and different requirements. Thus, for example, a quartz vessel is a suitable container for a tin melt but cannot be used with molten gallium.

Broadly described, the method of the present invention comprises the steps of running a clean niobium, or niobium alloy, or vanadium wire into a bath of molten tin or aluminum, gold or gallium and thereby forming an intermediate alloy layer on the wire, and then withdrawing the wire from the bath and cooling the wire and solidifying the adhering molten metal of the bath on the said intermediate alloy layer on the wire. This, accordingly, is a continuous and a comparatively rapid method of producing a superconducting wire which can be treated to develop a high current-carrying capacity and high quality in terms of its electrical and physical properties over its entire length. As indicated above, this coated niobium, niobium alloy or vanadium wire may be subjected to heat treatments to develop or enhance the special properties desired in it and these heat treatments may suitably be carried out continuously on the freshly-prepared coated wire or may be conducted at some much later time with the same results.

In the drawings accompanying and forming a part of this specification:

FIGURE 1 is a diagrammatical view of a wire-cleaning operation for the preparation of niobium and vanadium wires to be used in accordance with this invention in the manufacture of superconducting wires;

FIG. 2 is a semi-diagrammatic view of apparatus for processing wire emerging from the cleaning operations of FIG. 1 to provide it with a coating of tin or the like and the essential intermediate alloy layer; and

FIG. 3 is a chart on which critical current and current density are plotted against magnetic field for a tin-coated niobium wire produced by the method of this invention.

Where tin is the coating metal, the process of this invention will involve maintaining the molten tin at a temperature between 650° C. and 1300° C. throughout the period of the coating operation. Preferably, the temperature will be in the narrower range of 850° C. to 1100° C., and in actual practice we desire to operate near 950° C. While 650° C. represents the lower limit for operability, the essential reaction to produce the Nb_3Sn intermediate layer not going forward at substantially lower temperatures, the 1300° C. upper limit is not an absolute one but a practical one. At temperatures substantially higher than 1300° C., the tendency for the substrate wire of niobium or niobium alloy to soften and break becomes rather marked. Furnace windings also become a problem in such higher temperature operations.

The neutral atmosphere in the case of tin coating is any atmosphere which does not react to a material extent with either the freshly-prepared niobium or niobium alloy wire surface or with the molten tin. Argon and helium are preferred for this purpose and vacuum may also be used, but hydrogen is detrimental because it tends to embrittle niobium. The most important thing is to exclude free oxygen and free nitrogen from contact with

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the freshly-prepared substrate wire and the tin melt while the coating process is in operation, these being the principal common deleterious gases in terms of the properties of the ultimate wire product.

The temperature range in the case of gallium is the same as that of tin but that of aluminum varies slightly because the melting point temperature of aluminum is 660° C. Likewise, the range for molten gold is different, the melting point temperature of gold being 1060° C. In these cases, the ranges and preferences are as follows:

Gallium	650-1300, preferably 950
Aluminum	660-1300, preferably 950
Gold	1060-1300, preferably 1100

° C.

In reference to the drawings, in FIG. 1 a niobium wire 10 in the form in which it is obtained on the open market is cleaned in four stages, first being introduced into a bath 12 of a mixture of hydrofluoric and nitric acids in vessel 13. This mixture consisted of 110 cc. of concentrated (70% by weight) nitric acid in 3000 cc. of concentrated (52% by weight) of hydrofluoric acid. Running continuously, wire 10 is withdrawn from bath 12 and introduced into bath 15 of (52% by weight) hydrofluoric acid in vessel 16 and then rinsed in a body of water 17 in vessel 18. Following the water rinse, the wire is run through acetone 19 in vessel 20 and wound on reel 21. The rate of travel of the wire from reel 11 through the four cleaning stations to reel 21 is such that each successive segment of the wire remains in contact with each of the liquid bodies for about 5 seconds.

A molten bath of tin 24 is contained in a quartz vessel 25 that is generally tubular and channel-shaped in transverse section with its open ends disposed above the level of bath 24. The entry end 26 of vessel 25 is provided with a quartz closure piece or stopper 28 in which is fitted a gas delivery line 29 for the purpose of introducing gas continuously into chamber 30 between closure 26 and the surface of bath 24. Closure 26 is also provided with an opening through which clean niobium wire 10 may be run continuously in travel into vessel 25 and through which gas may escape from chamber 30 in continuous counterflow to wire 10. Discharge end 32 of vessel 25 is similarly fitted with a closure element 34, which is like closure piece 26 and is therefore fitted with gas delivery line 35 having an outlet end within chamber 37 between the inner end of closure piece 34 and the upper surface of bath 24. Also a small aperture is provided in closure piece 34 through which gas may flow continuously to prevent access of air to chamber 37, and also through which coated niobium wire may be continuously withdrawn from vessel 25.

Guides 38 and 39 are integrally formed with the body of vessel 25 and located within the vessel to engage wire 10 and maintain it in spaced relation to the vessel wall between these guides as illustrated in FIG. 2. By virtue of this construction and operation, the tendency for the wire to drag-out melt and form deposits on the vessel above the bath surface is avoided and the problem of wire breakage due to hang-up on such deposits is solved. Niobium wire 10 on reel 21, having been freshly-cleaned, is run through molten tin bath 24 continuously and collected on reel 40, the wire running through closure piece 26 into chamber 30 and then through bath 24 and chamber 37. The rate of travel of wire over this course will preferably be substantially constant and suitably from 5 to 20 feet a minute, although much greater speeds are possible. The resident time of the wire in the bath maintained at a temperature from 650° C. to 1300° C. will under this condition be sufficient to assure consistently high quality superconducting properties in the ultimate product. Also, the resident time of the coated wire in chamber 37 will be adequate to freeze adhering tin on the niobium wire so that clearance of the coated wire in the closure piece aperture is not critical to the production of

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a uniformly coated product. Thus, those skilled in the art will recognize that time, temperature and the length of the travel course through the melt and through the cooling zone are interrelated in terms of the kind of product that is obtained. In general, the lower the melt temperature, the longer the substrate-melt contact period for a given thickness both of coating and of alloy intermediate layer. Consequently, in the practice of this invention process, the operator has a comparatively wide latitude of choice as to melt temperature, melt vessel design and substrate wire travel rate for any given coated wire product specifications.

The following example of the method of this invention as it has been used in practice or as it may be employed in variations of that practice are set forth below for purposes solely of illustration and not by way of limitation:

Example I

A 1900 foot length of 0.005 inch diameter niobium alloy core wire containing 1 percent zirconium was acid cleaned, as described above in reference to FIG. 1, washed in water and acetone and passed at a rate of 6 feet per minute through a 900° C. molten tin bath protected by argon. The apparatus employed was that of FIG. 2 and the bath or melt travel course of the wire was 2 feet long so that the resident period of the wire in the melt was 20 seconds. The superconducting properties were measured before and after heat treatment by measuring the critical current required to quench the superconducting state when tested in a field of 25,000 gauss and at 4.2° K. The following properties were obtained on short lengths of wire:

Critical current, I_c (amps)
at 25,000 gauss

- | | |
|---|-----|
| (1) As tin-dipped .005" dia. wire | 0.3 |
| (2) 1 hour at 220° C. + 11 hours at 950° C. in vacuum (10^{-3} Torr) | 10 |

Additional tests were made on the heat treated hairpin sample (a short length of wire bent into a U-shape) in fields up to 90,000 gauss. These results are plotted in FIG. 3 and represented by Curve A. The critical current density of the wire was 24,000 amps per square centimeter in a field of 90,000 gauss.

A solenoid of 10,400 turns was made with this heat treated wire. After tin-dip coating, the wire was insulated with $Mg(OH)_2$ and Lucite, wound onto a stainless steel coil form and heat treated for 10 hours at 935° C. in argon. A field of 39,500 gauss was generated in the solenoid at 4.2° K. The wire carried 6.8 amps at the peak field of 39,500 gauss before becoming normal resistive. This result is indicated at B in FIGURE 3.

Having thus described this invention in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it appertains to make and use the same, and having set forth the best mode contemplated of carrying out this invention, we state that the subject matter which we regard as being our invention is particularly pointed out and distinctly claimed in what is claimed, it being understood that equivalents or modifications of, or substitutions for, part of the specifically-described embodiments of the invention may be made without departing from the scope of the invention as set forth in what is claimed.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The continuous method of making a superconducting wire having a high current-carrying capacity which comprises the steps of continuously running a clean wire of metal selected from the group consisting of niobium and niobium-base alloys lengthwise into and through a bath of molten tin at a temperature between 650° C. and 1300° C. and thereby providing a tin coating on successive longitudinal segments of the wire and simultaneously forming an intermediate layer of Nb_3Sn on successive longitudinal segments of the wire, continuously removing

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the resulting tin-coated and Nb₃Sn covered wire lengthwise from the tin bath into a neutral atmosphere and cooling and freezing tin adhering to successive segments of the wire as the wire is traveled lengthwise through the neutral atmosphere, and continuously withdrawing the resulting superconducting wire product lengthwise from contact with the neutral atmosphere.

2. The method as described in claim 1 in which the resulting wire product is heat treated to increase the Nb₃Sn layer thickness and thereby improve the current-carrying capacity of the wire product.

3. The method as described in claim 1 in which the wire is niobium-one percent zirconium, the neutral atmosphere is argon, the temperature of the molten tin bath is about 900° C. and successive segments of the wire are traveled through the molten tin bath in approximately 20 seconds.

4. The method as described in claim 1 in which the wire is niobium-zirconium alloy and the resulting wire product is subjected to a temperature of about 950° C. for a period of time to increase the thickness of the Nb₃Sn layer and thereby substantially improve the current-carrying capacity of the wire product.

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