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Diepers

[11] **3,890,701**

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[54] **PROCESS FOR THE PRODUCTION OF A COMPOSITE WIRE HAVING AN ALUMINUM CORE AND A NIOBIUM COVER**

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[30] **Foreign Application Priority Data**

June 22, 1973 Germany 2331925

[52] **U.S. Cl.** ..... **29/599**; 29/624; 29/DIG. 11; 174/126 CP

[51] **Int. Cl.** **H01v 11/14**

[58] **Field of Search** ..... 29/599, DIG. 11, 624; 174/126 CP, DIG. 6

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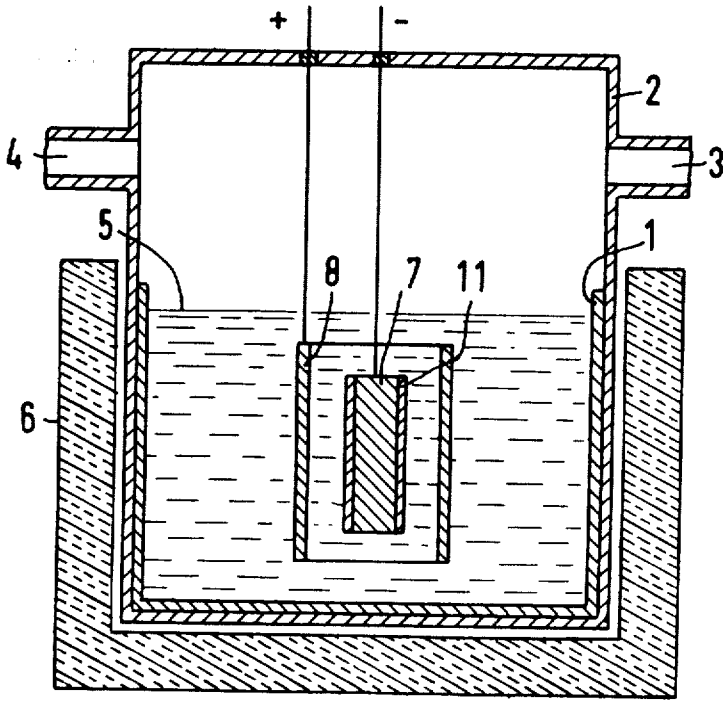
[57] **ABSTRACT**

A process for the production of a composite wire having an aluminum core and niobium cover surrounding it, the composite wire being produced from a starting rod having an aluminum core in the form of a rod with a hollow niobium cover surrounding it, which starting rod is drawn down using a drawing aid through a plurality of cold drawings until a strong bond between the aluminum and niobium is obtained and in which the composite so formed is subjected to a surface cold deformation after the removal of the drawing aid. In such a method, the present invention provides an improved manner of producing the starting rod in which a carrier is covered with a layer of niobium through fusion electrolysis after which the carrier is removed and the niobium tube formed in that manner then pushed on an aluminum rod of suitable diameter.

5 Claims, 4 Drawing Figures



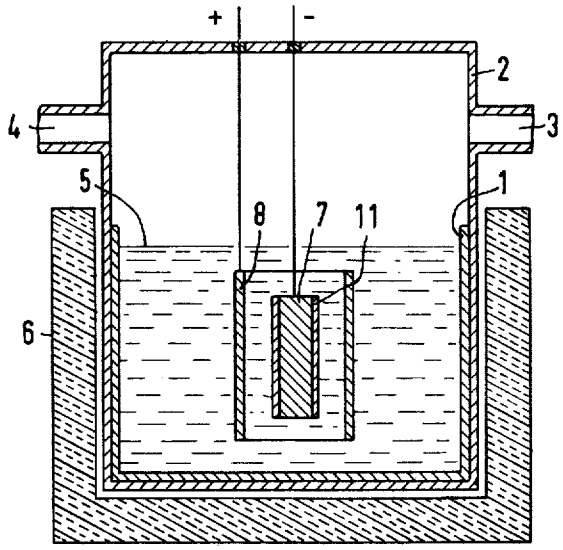


Fig.1

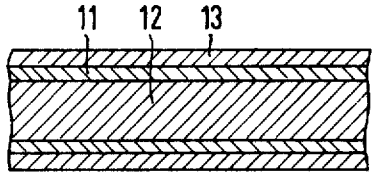


Fig. 2

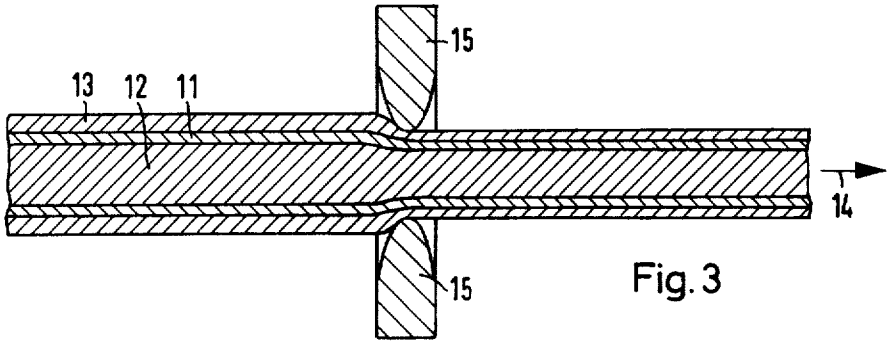


Fig. 3

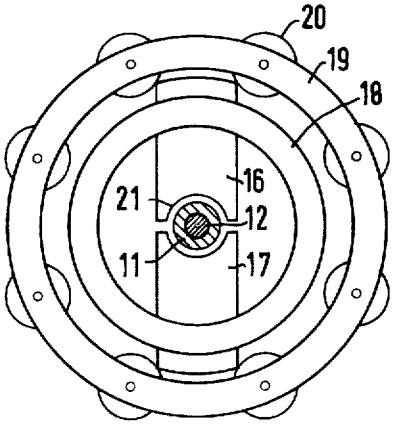


Fig. 4

PROCESS FOR THE PRODUCTION OF A COMPOSITE WIRE HAVING AN ALUMINUM CORE AND A NIOBIUM COVER

BACKGROUND OF THE INVENTION

This invention relates to the formation of composite wires of aluminum core with a niobium cover surrounding the aluminum in general and more particularly to an improved method of producing a starting rod comprising an aluminum rod surrounded by a cylinder of niobium which may then be cold formed to obtain a composite wire.

A method for the production of a composite wire having an aluminum core with a niobium cover surrounding the core is disclosed in U.S. Pat. application No. 378,423 filed July 12, 1973 and assigned to the same assignee as the present invention. In the process disclosed therein, an initial or starting rod is first formed from an aluminum rod serving as a core with a niobium cover surrounding the core. The initial rod is then drawn down through a plurality of cold drawing steps until a strong bond is obtained between niobium and aluminum. During cold drawing, a drawing aid is used surrounding the niobium cover. The composite object then has the drawing aid removed and as a final stage of operations is subjected to a surface smoothing cold deformation.

This disclosed process permits a simple means of producing the composite wire obtaining at the same time good super-conductivity characteristics, in particular, small a-c losses from the niobium cover. This latter feature is important where the composite wire is to be used in the superconductive cable, particularly a-c superconducting cables for which purpose niobium has been recognized as being an extremely suitable superconductive material. The aluminum at the operating temperature of the cables, i.e., about 4.2K is a good electric and heat conductor serving to provide electrical stabilization of the superconductive niobium. Aluminum provides significant advantages, particularly in a very pure form since it is relatively light in weight and at low temperatures has a particularly low specific resistance.

In the disclosed process, the production of the initial rod is accomplished by pushing a round aluminum rod into a niobium tube of suitable inner diameter and made of solid niobium. It is an object of this invention to provide an improved process of forming the starting rod which is used in the process of this prior patent application to obtain a composite wire. A further object of this invention is, to provide a starting rod which is improved in comparison with the starting rod disclosed in this prior patent application with regard to its further workability and to the superconductivity characteristics of the niobium cover.

SUMMARY OF THE INVENTION

In accordance with the present invention, the formation of the starting rod is accomplished by first covering a carrier with a layer of niobium in the form of a cylindrical coat using fusion electrolysis. After removal of the carrier, the niobium tube so formed is pushed on to an aluminum rod of similar diameter. The niobium obtained through fusion electrolysis is very pure and finely crystalline, with a columnar crystalline structure. This makes it very easy to shape mechanically thus

making it particularly suitable for use in the above described process for production of composite wire through a series of cold drawing operations. In addition, niobium obtained through fusion electrolysis has excellent superconductivity characteristics and in particular, has very small a-c losses. In accordance with the present invention, the cylindrical layer of niobium over the carrier is advantageously turned on a lathe prior to removal of the carrier.

Disclosed as carriers on which the layer of niobium can be deposited are suitable metals resistive to the fusion electrolysis electrolyte and which react as little as possible with niobium. In addition, such metals must have a melting point high enough that they do not melt in the molten electrolyte. Thus, aluminum because of its relatively low melting point of 659° is not suitable since the fusion electrolysis electrolyte is at a temperature of 740°C during electrolysis. A particularly suitable carrier is a carrier made of copper. Copper is resistant to the electrolyte, has particularly no reaction with the deposited niobium and is easily machinable and easily removed. Typically, the carrier may be removed by boring it out of the cylindrical casing layer of niobium or even by dissolving it out chemically.

As disclosed, when copper is used as a carrier, it is desirable after removal thereof to remove, using a lathe, a layer approximately 0.1 mm thick from the inside of the niobium case. This results in the removal of a thin interdiffusion layer between the niobium and copper which can be formed during the deposit of niobium and which might impair the superconductivity characteristic of the niobium.

As a particularly advantageous method of carrying out the fusion electrolysis, a method disclosed in an article by Mellors and Senderoff in "Journal of the Electrochemical Society," vol. 112, pages 266 to 272 is recommended. In general, the further processing of the starting rod after the aluminum rod is inserted within the niobium casing follows that disclosed in the above referenced patent application.

Various drawing aids are disclosed such as a copper tube surrounding the niobium outer layer. In particular, a tube of unannealed copper is recommended. This is left on during all of the cold drawing stages and removed only before final surface smoothing. Removal is done chemically. In well known fashion, in accordance with the strict requirements for cold drawing, drawing oil is also applied to the surface. Also mentioned as suitable drawing aids are a lacquer slip surface or a niobium pentoxide layer formed by anodic oxidation of the surface of the niobium. Although these may be used, they suffer from the disadvantage that they must be renewed after only a few drawing operation steps and must be removed again prior to the final surface smoothing operation.

In accordance with the present invention, it is desirable that the surface of the aluminum rod be etched before it is pushed into the niobium tube obtained by fusion electrolysis. The number of cold drawing steps necessary to obtain a strong bond between niobium and aluminum can be determined in individual cases by experimentation. A sufficiently strong bond is indicated when, during further cross section diminishing operations, aluminum no longer is squeezed out at the ends of the niobium case. Typically, this will occur after a decrease in the initial cross section of approximately 20 percent. Although this reduction of cross section can

be obtained in a single drawing step, it is preferable to employ a number of drawing steps in order to carefully treat the niobium surface. Even after the firm bonding has taken place, further drawing steps may be carried out to draw the rod down to a wire of the required size. It is particularly advantageous that the composite wire in a final surface smoothing step be round hammered. This insures a very smooth surface of the niobium case and at the same time compacts the niobium. This in turn leads to a high critical current density for the niobium which is particularly important during the operation at times when the lower critical magnetic field H_{c1} is exceeded. In addition, the round hammering improves the bonding between the niobium and aluminum. In the disclosed method of round hammering, the composite is rotated about its longitudinal axis relative to the hammer jaws.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of an apparatus for coating the carrier by means of a fusion electrolysis.

FIG. 2 is a longitudinal cross sectional view of an initial rod including a niobium cover case into which an aluminum rod is inserted and over which a drawing aid is placed.

FIG. 3 is a schematic illustration of the production of a composite wire or rod to the cold drawing of the initial rod of FIG. 2.

FIG. 4 is a schematic end view illustrating the final step of cold hammering of the composite rod or wire.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

FIG. 1 illustrates schematically the apparatus of carrying out the fusion electrolysis coating of a copper carrier with niobium. In accordance with the present invention, there is first placed into a container 1 preferably made of nickel, the constituance of the electrolyte. As noted above, electrolysis is preferably carried out using the process as described by Mellors and Senderoff in the Journal of the Electrochemical Society, vol. 112, pages 266 to 272 [1965.] A particularly suitable electrolyte is a eutectic mixture of sodium fluoride, potassium fluoride and lithium fluoride in which is dissolved potassium heptafluoroniobate [K_2NbF_7]. The detailed composition of the electrolyte is by weight as follows: 16.2 percent K_2NbF_7, 26.2 percent LiF, 10.4 percent NaF and 47.2 percent KF. As illustrated, an electrolyte container 1 preferably made of nickel is situated within the lower part of a coating chamber 2 which is preferably made of high grade steel. After this, the coating chamber is evacuated using tubular connectors 3 and 4 whereupon an inert gas such as argon is passed therethrough. The electrolyte 5 is then heated through the use of an electric resistance heater 6 which surrounds the lower part of the coating chamber 2. It is heated to approximately 740°C to cause the electrolyte to melt. The copper carrier 7 to be coated, for example, a copper rod having a diameter of about 20 mm and an anode 8, for example, a sheet of niobium concentrically surrounding the copper carrier 7 are then put into the molten electrolyte 5. With this arrangement, the copper carrier acts as a cathode. Prior to immersion of the electrodes into the electrolyte, a preliminary deposit on an auxiliary cathode may be carried out in the manner described in German Offenllegungsshrift 2,114,555. Furthermore, it is desirable as described in detail in German Offenlegungsshrift 2,115,179 to surround the cathode with a fine mesh screen made of a material resistant to the fusion electrolysis electrolyte and to dispose the anode outside of the screen. By doing so, disturbing influences of slag-like impurities are avoided. Under certain conditions, these could get in to the fusion electrolysis electrolyte and have deliterious effects. This Offenlegungsschrift further discloses apparatus for carrying out such electrolyte coating in more detail than it is shown for reasons of clarity, in FIG. 1. This apparatus and other similar apparatus is well known to those skilled in the art.

A voltage of polarity as shown is then applied to the electrodes with the voltage of sufficient magnitude to establish a current density of approximately 40 ma/cm² on the cathode. With this current density and the above described electrolyte and with an electrolyte temperature of approximately 740°C, a thickness of approximately 0.6 μm of niobium per minute is deposited on the copper carrier. Deposition can advantageously be continued until a layer of approximately 2 mm in thickness is deposited on the copper carrier 7 having a diameter of approximately 20 mm. The copper carrier preferably will be in the form of a rod and will be immersed into the electrolyte to a sufficient depth so that a cylindrical layer of niobium having length in the axial direction of approximately 50 cm will be formed. After coating, the copper carrier is removed from the electrolyte, allowed to cool under a protective gas and is then removed from the coating chamber. After this, it is preferred that the deposited niobium layer be finely lathe turned on the outside for the purpose of smoothing its surface. The copper carrier is then removed by first drilling a central hole therethrough and then using a lathe, turning from the inside toward the outside, to remove the copper. After complete removal of the copper carrier, a 0.1 mm layer of niobium is preferably removed by the lathe in order to insure removal of any interdiffusion area present.

This results in a niobium tube 11 such as that shown on FIG. 2, which tube has been formed by fusion electrolysis. It will thus have the advantageous characteristics noted above. The niobium tube 11 is then pushed onto an aluminum rod having a diameter of approximately 19 mm and a length of 50 cm. It is recommended that the aluminum rod 12 be etched with hydrochloric acid prior to insertion. Over the outside of the niobium tube which will have a diameter of about 24 mm an unannealed copper tube having an inner diameter of about 26 mm and a wall thickness of about 1 mm is pushed for use as a drawing aid. Prior to placing the tube of copper over the niobium, it should be etched in dilute nitric acid for cleaning purposes.

The initial rod so formed is then cold drawn in a number of cold drawing steps as illustrated in FIG. 3 to reduce it to a composite rod of smaller diameter. In a preferred method of carrying out the present invention, cold drawing is carried out until the diameter of the niobium case 11 is reduced to approximately 2.25 mm. Preferably, this is done by reducing the cross section 10 percent during each drawing step. A drawing speed during the first step, at which speed the starting rod is pulled through the die 15 in the direction of the arrow 14 of FIG. 3, can be approximately 14 m/minute. Thereafter, for further drawing steps, the speed may be increased to 20 m/minute. For facilitating the drawing operation, a layer of commercial drawing oil is applied

over copper tube. After only two or three drawing steps, a firm bond between the niobium and aluminum will have been produced. Also suitable as drawing aids are a lacquer slip surface applied over the niobium case or a niobium pentoxide layer formed by anodic oxidation of the surface of niobium case. Typical of a lacquer slip surface is one made of Zapon varnish or some other quick drying nitro-cellulose lacquer. However, if lacquer or niobium pentoxide layers are used rather than the copper tube, these layers must be renewed after a few drawing operations. In addition, the layers just as the copper tube must be removed prior to the final surface smoothing operation.

After the final drawing step, the copper covering is removed using nitric acid. This leaves only the aluminum core **12** and niobium case forming a composite wire. This composite wire is illustrated by FIG. **4** being treated in the final operation of round hammering in a round hammering machine. The general construction of the round hammering machine is illustrated. It includes hammer jaws **16** and **17** supported resiliently for radial travel within an annular mount **18.** The annular mount **18** rotates along with the hammer jaws **16** and **17** inside an annular ring **19** which rotates at half the rotary speed of the mount **18** and has thereon a set of rollers **20.** As the hammer jaw **16** and **17** rotate past the rollers, they are passed inward in the mount **18** and hit the surface of the niobium case **11** of the composite wire. The surfaces of the jaws **16** and **17** of the hammers which hit the niobium case have a rounded slot or groove **21** of substantially semicircular cross section which may advantageously be tapered down, at least slightly, in the direction in which the composite wire advances. The speed at which the wire advances between the hammer jaws **16** and **17** will be, for example, 2 meters/minutes. In this step, the prior outer diameter of 2.25 mm present after the last drawing step is hammered down to about 2 mm. Preferably, the hammer jaws **16** and **17** can be adjusted to strike the composite structure about 4,500 times a minute while turning around the composite structure at several hundred revolutions per minute. The composite structure was turned about its axis 15 times per minute during that period. This insures that the composite object continuously changes its position relative to hammer jaws thereby becoming well rounded and smooth. Moreover, the slow turning also prevents the rapidly rotating hammer jaws from leaving traces on the surface of the wire as it hits the composite wire. From this step, the surface of the niobium case of the composite wire, which upon removal of the copper case after the final drawing step was somewhat undulated, now becomes completely smooth through the round hammering.

A finished composite wire manufactured according to the present invention was tested to determine its a-c losses in the niobium layer, the contact resistance between the niobium and aluminum, and the residual resistance ratio of the aluminum, i.e., the quotient of the ohmic resistance of aluminum at 300K and the ohmic resistance of aluminum at 4.2K. Prior to processing the aluminum rod had a residual resistance ratio of about 2,500. In the finished composite wire the residual resistance ratio had decreased to a value of about 1200, a value which is still quite high. Such a residual resistance ratio is quite adequate when the composite wire is to be used in a superconductive cable and annealing of the composite is not necessary. By eliminating an annealing step, a further advantage is obtained in that it avoids an undesirable formation of a very brittle intermetallic phase of $NbAl_3$ in the contact zone of the niobium and aluminum. Thus, with this process, such an intermediate layer, which is easily formed at higher temperatures, is not present and is not caused to be formed during the cold forming steps used. Even without an actual annealing treatment at high temperature, the residual resistance ratio of the aluminum may still be surprisingly increased to a value of about 2,000 through a brief heating of the composite wire to between 50° and 100°C for approximately 5 to 30 minutes.

The contact resistance measured between the niobium and aluminum was quite low, i.e., about 3×10^{-8} ohms. cm. This low contact resistance also shows how intimate the bond between the niobium and aluminum is. A-C losses of the niobium case as long as the lower critical field of the niobium of approximately 10^5 A/m is not exceeded are also very low. With an A-C frequency of 50 Hz a loss of somewhat less than 0.1 μw per cm^2 of wire surface was experienced in the niobium case formed by fusion electrolysis according to the present invention.

In addition to the advantages described above regarding the good mechanical deformability and good superconductive characteristics of the niobium case obtained through fusion electrolysis, the process of the invention has all of the advantages described in connection with the above referenced application. The cold drawing insures an intimate bond between the niobium case and aluminum core. This results in small contact resistance between the niobium and aluminum. This is of particular and decisive importance for a good electrical stabilization of the niobium case by the aluminum core. As aluminum has a greater coefficient of expansion under the action of heat than does niobium, strong bonding between the two materials is essential so that the niobium case does not break away from the aluminum core during cooling down from room temperature to the operating temperature of a superconductive cable of approximately 4.2K. In addition, a smooth niobium surface keeping a-c losses of the niobium, which are closely dependent on its surface characteristics, quite small is obtained through the final processing step. Thus, it is clear that the composite wire obtained in accordance with the present invention provides an excellent wire for use in a conductor in a superconducting a-c cable.

Thus, a process for producing an improved composite wire has been described. Although specific steps have been disclosed, it will be obvious to those skilled in the art that various modifications may be made without departing from the spirit of the invention which is intended to be limited solely by the appended claims.

What is claimed is:

1. In a low temperature process for producing a composite wire having an aluminum core and niobium case surrounding the core without submitting the composite wire to any temperature above about 100°C., in which process an initial rod is produced from a rod-like aluminum core with a niobium case surrounding the core after which the initial rod is reduced in cross section by a plurality of cold drawing steps, with a drawing aid applied to and surrounding the niobium case, thereby obtaining an intimate mechanical bond between the niobium and aluminum, with the final step comprising a surface smoothing cold deformation carried out after

removal of the drawing aid, an improved process for forming the initial rod for use in making the composite rod comprising:

a. coating a carrier with a niobium layer by fusion electrolysis to form a cylindrical case of niobium over the carrier;
b. removing the carrier to leave only the niobium case; and
c. pushing an aluminum rod of suitable diameter inside the niobium case.

2. The method according to claim **1** wherein said carrier is copper.

3. The method according to claim **2** and further including the step of removing a layer of approximately 0.1 mm from the inside of the niobium case after removal of the carrier.

4. The method according to claim **1** wherein the niobium case is smoothly lathe turned on the outside prior to removal of the carrier.

5. The method according to claim **4** wherein said carrier is copper.

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