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METHOD OF PRODUCING A BODY WITH EMBEDDED SUPERCONDUCTING METAL FILAMENTS

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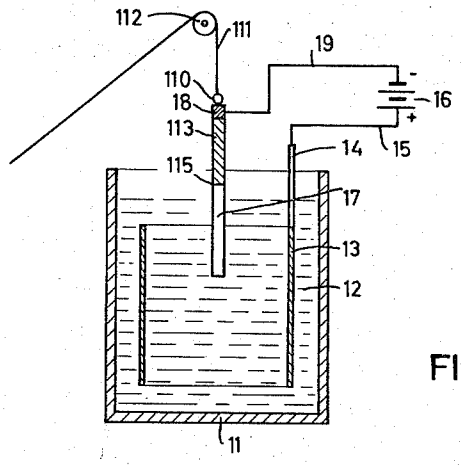


FIG. 1

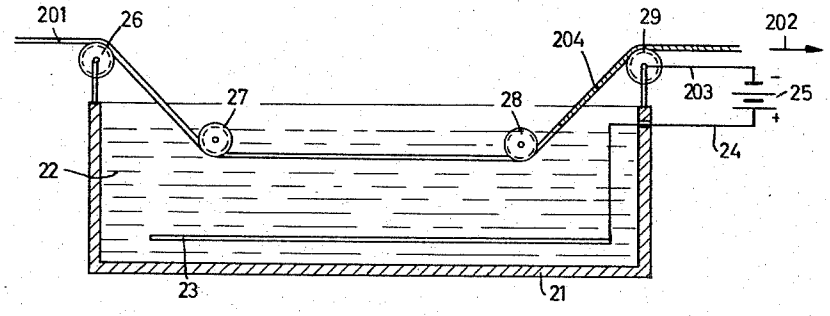


FIG. 2

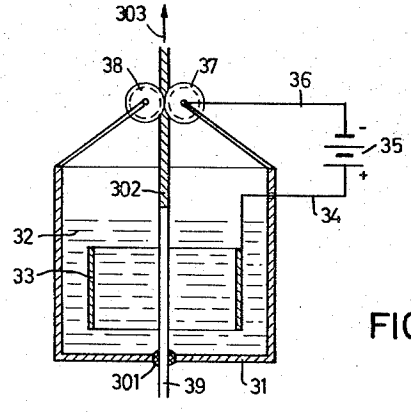


FIG. 3

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METHOD OF PRODUCING A BODY WITH EMBEDDED SUPERCONDUCTING METAL FILAMENTS

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9 Claims. (Cl. 204—20)

ABSTRACT OF THE DISCLOSURE

Method of producing electric conductor members having embedded filaments of superconductive metal described. Porous body having intercommunicating pores is immersed into electrolytic bath containing ions of superconducting metal. Voltage applied between cathode contacting the body outside the bath and anode within bath through electrolyte drawn into pores by capillary action. As a result, filament-shaped deposits of the metal within electrolyte form in pores.

My invention relates to a method of producing an electric conductor member for utilization of superconductance by operation at cryogenic temperatures.

The particular behavior of hard superconductors in magnetic fields of high field strength has been explained theoretically by the so-called "filament" model. According to this theory, when the so-called hard superconductors, constituted by metals in elemental form or as alloys, are subjected to very high external magnetic fields dominating over the thermodynamically critical field, superconductance will still persist in thin filament-like zones while large volumetric portions of the material have already converted to normal conductance on account of the high external field. It is assumed that these superconducting filaments are intermeshed and thus form a coherent network.

K. Mendelssohn (Proc. Roy. Soc., 152A, 1935, 34) attempted to characterize the structure of such a network by comparison with a sponge. What causes the sponge-like "filament" mesh regions to still remain superconductive in high magnetic fields when the other regions in the material have already turned normal, it not yet clearly understood. It is being theorized that these "filaments" may coincide with dislocations, or may correspond to inhomogeneities in the atomic or molecular structure of the metallic material, or may constitute regions with a negative surface energy. Many diversified physical investigations have been undertaken but so far have failed to permit deciding between these different concepts. In this connection, it has been attempted by Bean, Doyle and Pincus (Phys. Rev. Letters 9, 1962, 93) to create an artificial "filament" structure by pressing mercury, a "soft" superconductor, into a porous rod of quartz glass at 3,300 atm. hydrostatic pressure and normal room temperature. After reducing the pressure, some of the liquid mercury again emerged out of the rod within a period of a few minutes, due to the high surface tension of mercury and the absence of wetting in the pores. By cooling the rod to below the melting point of mercury, the authors were able to keep a portion of the original mercury quantity in the rod. Specimens thus prepared were subjected to magnetizing test at 2.16° K. It was found that the specimens exhibited magnetization curves as typical for hard superconductors, in contrast to solid mercury in wire or rod shape which behaves as a typical soft superconductor. The difference in behavior

was explained by the "filament" structure formed by the arrangement of the mercury within the pores of the quartz-glass rod.

These experiments raised the question whether bodies of such a structure can be produced also on a technological or industrial scale. It was immediately ascertained that it is extremely difficult and intricate to press mercury into a body under such a high hydrostatic pressure as 3,300 atm., and that a method of this type would be limited to bodies of relatively small dimensions and to the use of liquid metals. It is also a requirement for technological applicability that such bodies must be capable of conducting electric current applied from the outside. This is virtually infeasible when applying the above-mentioned pressing method because, when the pressure is being reduced, a portion of the impressed mercury again emerges from the body since mercury tends to contract with droplet formation. Most of the coherent filaments then tear into short fragmentary pieces. While this does not impair the magnetizing properties of the specimens, it eliminates the through passages required for a current to be supplied from an extraneous source.

It is, therefore, an object of my invention to devise a method that permits the production of electric conductor members in which a porous carrier body is provided with embedded filaments of superconductive metal, so that these filaments reliably form through passages and thus permit using the body at cryogenic temperatures for utilization of superconductance that will remain effective even if the conductor body is simultaneously subjected to magnetic fields of a high intensity above the normally critical value.

Another, more specific object of the invention is to provide a method that affords in a simple manner to introduce any desired metals into a porous carrier body, and which further affords the reliability that current-conducting filaments of the metal are formed within the body for use of the body at temperatures in the superconductance range as a conductor for current from an extraneous source.

According to my invention, the desired superconducting filaments of metals, this term being herein understood to mean metals in the narrower or elemental sense as well as alloys, are embedded into a porous carrier body by an electrolytic method performed in the following manner. The porous body to be provided with embedded metal filaments is so chosen or prepared that the pores merge with one another so as to form passages. Such a porous body is immersed with a cathode into an electrolytic bath containing the ions of the metal of which the filaments are to consist. A voltage is applied between the cathode and a likewise immersed anode so that the metal is electrolytically precipitated into the pores of the body to form filaments therein.

The porous bodies used for this method may be given any desired shape, for example that of a prism, an elongated rod of round or other cross section, a hollow or tubular body, or the shape of a wire of any desired length.

A deposition of metal takes place only at such localities where an electrically conducting connection to the cathodic electrode exists. Commencing from the electrode, the metal precipitates in form of filaments in the filament-like through-passages formed by the pores of the carrier body. Consequently when the metal deposition extends throughout the length of the passages, the resulting filaments are capable to conduct electric current through the body. By virtue of the fact that different metals can be chosen, the physical values of such a conductor component can be varied and adapted in a convenient manner. If desired, ions of respectively different

metals may be simultaneously present in the electrolytic bath. As a result, a corresponding alloy is precipitated in the pores of the carrier body. The electrolytes to be employed in a particular case may correspond to the compositions known for the respective metals. However, a number of preferred electrolyte compositions will be described further below in this specification.

The method of the invention is applicable to all electrolytically precipitatable and superconducting metals, for example tin, lead or lead-tin alloys. Particularly advantageous is the use of metals having a high transition temperature, such as niobium, rhenium, lead-bismuth or niobium-zirconium. (For other applicable superconductive materials, transition temperatures and critical magnetic fields, reference may be had, for example, to "Superconductivity" and the literature mentioned in the appertaining bibliography, on pages 295 to 301 of volume 13, McGraw-Hill Encyclopedia of Science and Technology, New York, 1960.)

Suitable as porous carrier bodies are particularly unglazed porcelain or similar ceramic material, rigid or bendable synthetic plastic foam materials, such as polystyrene- or polyester-foam materials, also bodies sintered from metal powders of very poor electric conductivity, for example surface-oxidized metals such as oxidized aluminum or iron powder, as well as sintered bodies of glass, or generally all materials having merging pores or through pores and a constitution resistant to the electrolyte being used. Sinter bodies of poorly conducting metal powders are particularly well suitable in cases where a high mechanical strength of the porous carrier bodies is required. Suitable as flexible or bendable porous carrier bodies, required for example in the production of superconducting wires or tapes, are particularly strings and tapes of wool or cotton threads because of the good wettability of such threads, or wires and tapes of synthetic flexible foam materials.

The conductor bodies made according to the invention exhibit high critical current densities in the cryogenic superconductance range and are free of eddy current losses when used with alternating current.

The preparation of the porous carrier bodies prior to electrolysis is substantially the same for the various materials. One end of the porous body is provided with an electrode or terminal which constitutes the original cathode. For this purpose a hole is drilled into the porous body either in the direction of its longitudinal axis or perpendicularly to this axis. A piece of wire is then inserted into the bore. This of course applies to rigid porous bodies. However, there are other ways of attaching the cathode terminal, not requiring a drilling operation. For example, the corresponding end of the porous body need only be covered by a metallic cap provided with a current supply terminal.

The porous bodies thus equipped with an electrode, are immersed into the electrolytic bath in which the counter electrode is also immersed. Due to capillary forces, the electrolyte ascends in the porous body. Consequently the liquid level in the interior of the porous body is higher than the level of the electrolyte in the electrolysis vessel. The elevation difference between the two liquid levels depends upon the pore side in the body.

If the pores of the body extends from the interior to the entire outer surface of the body, the metal also precipitates up to the surface. In this case, it is not necessary to attach an electrode firmly to the porous body, and the current can be supplied to the body with the aid of conducting rollers or rotating cylinders, particularly in cases where the porous carrier body is elongated such as in the shape of a rod, wire or tape. The supply of current by means of rollers is particularly advantageous for continuous precipitation methods.

When performing the electrolytic precipitation of metals with bodies whose pore openings are distributed over the entire body surface, care must be taken that the zone

in which the precipitation of metal within the pores takes place, remains located above the liquid level of the electrolytic bath in the vessel, so that the metal already precipitated in the pores near the surface of the body cannot touch the surface of the electrolytic liquid outside the porous body.

If no such care is taken, and if the metal precipitated at the surface of the porous body enters into direct contact with the bath surface outside the body, a metallic conducting bridge may be formed between the body and the surface of the bath. For example, tree-shaped dendrites of lead are formed in this manner when lead is being precipitated electrolytically. The metallic bridges may then assume the entire transportion of electric current between anode and cathode, and the electrolytic precipitation in the interior of the porous body will cease.

The precipitation zone, as a rule, can readily be maintained above the liquid level of the electrolyte in the processing vessel, because the liquid in the interior of the porous body ascends by capillary forces above the bath surface outside of the porous body. In general, the position of the precipitation zone can be observed by discoloration of the body surface caused by the precipitated metal. In order to preserve the just-mentioned condition during the entire course of the precipitation process, the porous body must be slowly pulled upwardly out of the electrolytic bath as the precipitation process progresses.

The precipitated metal need not fill the entire pore cross section, it being sufficient if a conducting connection comes about in the through-passages formed by the pores. The precipitated quantity of metal depends upon the electrolyte concentration, the pore size and the pulling speed, as well as upon the applied voltage.

Due to the relatively high resistance in the porous body, the voltage required for the electrolytic deposition is considerably higher than usually employed for normal electrolysis, for example electroplating. As a rule, a voltage of approximately 20 volts is preferable for the purpose of the invention. When the current is switched on, the electrolytic precipitation of metal commences at the cathode and advances in the pore direction within the body. The electrolysis is continued, while slowly moving the original cathode away from the bath, until the porous body is traversed by metallic filaments. The anodic counter electrode employed is preferably made of the same metal as the one to be precipitated from the electrolyte into the pores of the carrier body. Such an electrode of the same metal was used in conjunction with the compositions and tests described below.

Tested and preferred electrolyte compositions for the precipitation of tin, lead, rhenium, niobium, a lead-tin alloy and a lead-bismuth alloy will be described presently.

Tin

Tin-II-sulfate per liter solution ____g__	50
Conc. H_2SO_4 per liter solution ____g__	20
Bath temperature ____° C__	20

Lead

Lead as lead silicofluoride ($PbSiF_6$) ____g./l__	80
Free hydro-silicofluoric acid (H_2SiF_6)__g./l__	150
Bath temperature ____° C__	30 to 40

Rhenium

Potassium perrhenate ($KReO_4$) per liter solution ____g__	10
Conc. H_2SO_4 per liter solution ____g__	3
Bath temperature ____° C__	25

Niobium

Pulverulent niobium pentoxide dissolved in 1 liter KOH solution of 10% concentration _g__	12
Bath temperature ____° C__	90

Lead-tin alloy

Lead fluoroborate per liter solution ____g__	20
Tin fluoroborate per liter solution ____g__	20
Free fluoroboric acid per liter solution ____g__	40
Bath temperature ____° C__	20

Lead-bismuth alloy

Perchloric acid per liter solution ____g__	93
Lead per liter solution ____g__	18.6
Bismuth per liter solution ____g__	9.0
Bath temperature ____° C__	40

The method of the invention will be further described with reference to the accompanying drawing in which FIGS. 1, 2 and 3 show schematically and in section three different embodiments respectively of equipment for performing the method.

The apparatus shown in FIG. 1 is suitable particularly for precipitating superconducting metals in rigid bodies of various shape. A tank **11** contains the electrolyte liquid **12**. Immersed in the liquid is a preferably ring-shaped electrode **13** which is connected by a contact strip **14** and a lead **15** with the positive pole of a direct-voltage source shown as a battery **16**. The porous body **17**, here exemplified by an elongated rigid rod, has its upper end provided with a good conducting electrode **18** which is connected by a lead **19** with the negative pole of the voltage source **16**. The electrode **18** is provided with an insulated eye **110** to which a pull rope **111** is fastened. The rope runs over a roller **112** and permits immersing the porous body **17** into the electrolytic bath **12** and pulling the body gradually out of the bath. In FIG. 1 the portion **113** of the porous body in which metal is already precipitated, is identified by diagonal hatching. The precipitation zone at **115** is located above the level of the electrolyte **12** in tank **11**. The operation of the device will be further described below.

The apparatus illustrated in FIG. 2 is suitable for the electrolytic precipitation of superconducting metals in flexible wires or tapes of porous material having the pores at the entire surface. A trough **21** of elongated shape contains the electrolyte liquid **22** and an electrode **23** which is connected by a lead **24** with a direct-voltage source **25**. Mounted on the trough **21** are rollers **26**, **27**, **28** and **29** for the transportation of the porous strand-shaped body **201** through the electrolyte **22** in the direction of the arrow **202**. The roller **29**, positioned closely behind the location at which the porous body **201** emerges from the bath **22**, is designed as a rotatable brush contact and is connected by a lead **203** with the negative pole of the voltage source **25**, thus supplying electric current through the portion of the porous body **201** that already contains metallic filaments and extends between the roller **29** and the precipitation zone located somewhat above the level of the bath. The portion **204** of the porous body **201** already containing precipitated metal is identified by diagonal hatching.

The apparatus according to FIG. 3 is suitable for the precipitation of superconducting metals in flexible or bendable wire or tape-shaped bodies, or also in rigid rod-shaped bodies having pores at the entire surface. A tank **31** contains the electrolyte liquid **32** and a preferably ring-shaped electrode **33**. The electrode **33** is connected by a lead **34** with the positive pole of a voltage source **35** whose negative pole is connected through a lead **36** with a conducting roller **37** whose axis is fixed in relation to the position of the trough **31**. A second guide roller **38** presses the porous body **39** against the current-supply roller **37** and is driven during operation of the apparatus, preferably by a motor, in order to pull the porous body **39** through the electrolyte bath in the upward direction indicated by an arrow **303**. The body enters through a liquid-tight seal **301** in the bottom of the trough. The portion **302** of the porous body in which

metal is already precipitated, is identified by diagonal hatching.

For further elucidiating the invention, a specific processing example will be described presently.

Lead was to be precipitated in the pores of a rod consisting of sintered glass having a length of 10 cm. and a diameter of 0.5 cm. The precipitation was carried out with apparatus as shown in FIG. 1. The pores of the sintered glass rod **17** had a median diameter of 10 microns, the share of the pores in the outer volume of the rod was approximately 20 to 25%. One end of the glass rod was covered by a metallic cap **18**. In the example here described, a piece of copper tubing of matching diameter was pressed upon the end of the rod and then provided with an insulating eye **110** to which a pull tape **111** was fastened to run over the roller **112**. The lower end of the glass rod was then immersed into the electrolyte **12** to such a depth that the liquid ascending in the rod by capillary action was in contact with the electrode **18** then located above the level of the liquid. The electrolyte **12** used had the composition and temperature described above with reference to the production of lead filaments. The electrode **13** consisted of lead in metallic form.

After the rod was immersed into the electrolyte up to the depth just described, the electrodes **13** and **18** were connected with the voltage source **16** to be impressed with direct voltage of 20 v., the electrode **18** being connected to the negative pole and the electrode **13** to the positive pole. Upon completing the electric connection, the precipitation of lead into the pores of the sintered rod commenced at the electrode **18**. A current of about 70 ma. then passed through the electrolyte. The precipitation zone migrated in the rod at a speed of about 3 cm. per hour from the upper toward the lower end. In order to have the precipitation zone always located above the level of the electrolyte **12** in the tank **11**, the glass rod was lifted at the same speed out of the electrolyte with the aid of the pull tape **111**. The process was continued until the entire sintered rod was traversed by filaments of lead.

The precipitation of the other mentioned metals in porous bodies can be effected in the same manner with a corresponding choice of the electrolyte liquid and the material for the electrode **13**. A direct voltage of about 20 volts has been found sufficient for the precipitation of all of these metals.

With the aid of equipment, corresponding for example to that shown in FIG. 2 or FIG. 3, designed and operating substantially in analogy to equipment used for electroplating the precipitation of superconducting metals, in elemental form or in the form of alloys, can conveniently be carried out with porous bodies of any desired shape, for example with bodies of synthetic materials shaped as wires, tapes or other elongated configurations. When the pores of the material extend up to the surface, the metal also precipitates from the interior up to the surface, and the current for the cathode can then be supplied shortly above the bath with the aid of a contact roller or cylinder. Rigid bodies extending mainly in a single direction, for example bodies of porcelain or sintered glass, can be pulled longitudinally through liquid-tight seals into the vessel and through the electrolytic bath, as described. In this case, too, the cathodic current supply may be effected by means of a contact roller or by means of a cathode attached to the porous body, depending upon whether or not the pores are open at the surface of the body.

Conductor members having a porous carrier body and embedded superconducting metal filaments produced according to the invention, are applicable for alternating current as well as for direct current under superconductivity conditions.

The method according to the invention is further applicable for producing hollow cylindrical members of any desired proportions, for example those in which an annular flow of currents about the longitudinal axis is to be produced by means of induction, or in which high magnet-

ic fields are to be built up by the so-called magnetic pumping (P. Swartz and C. H. Rosner, Journ. Appl. Phys. 33, 1962, 2292).

The method of the invention also affords producing components of a complicated shape, for example for use in apparatus and machines to be operated in the condition of superconductivity, such as the rotors or stators for motors or generators. Bodies with embedded superconducting filaments made according to the invention are also applicable as material for magnetic shielding.

To those skilled in the art it will be obvious upon a study of this disclosure that our invention is amenable to a variety of modifications and variations with respect to processing detail, structural details of the bodies being produced, or the particular electrolysis equipment being employed, as well as regards the uses to which the produced bodies may be put, and hence that the invention can be given embodiments other than particularly illustrated and described herein, without departing from the essential features of the invention and within the scope of the claims annexed hereto.

I claim:

1. The method of producing an electric conductor member having embedded filaments of superconductive metal, which comprises immersing a non-conductive porous body having intercommunicating pores traversing the body, in an electrolyte bath containing ions of said metal; applying voltage between a cathode which contacts said body outside the bath and an anodic electrode in said bath, with contact between cathode and anode being through electrolyte capillarily drawn into the pores, and thereby electrolytically producing filament-shaped depositions of the metal from the electrolyte in the pores of the body.

2. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said porous body is formed of unglazed porcelain.

3. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said porous body is formed of synthetic plastic foam.

4. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said porous body is formed of sintered powder material.

5. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said porous body is formed of a sintered powder of surface-oxidized metal.

6. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said porous body is formed of sintered glass powder.

7. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said porous body is an elongated material formed of textile threads.

8. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said electrolyte contains essentially ions of one precipitating metallic element and the precipitated filaments consist of said element.

9. The electrolytic method of producing current conductor members with embedded superconductance filaments according to claim 1, wherein said electrolyte contains ions of a plurality of metallic elements, and the precipitated filaments consist of an alloy of said element.

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