

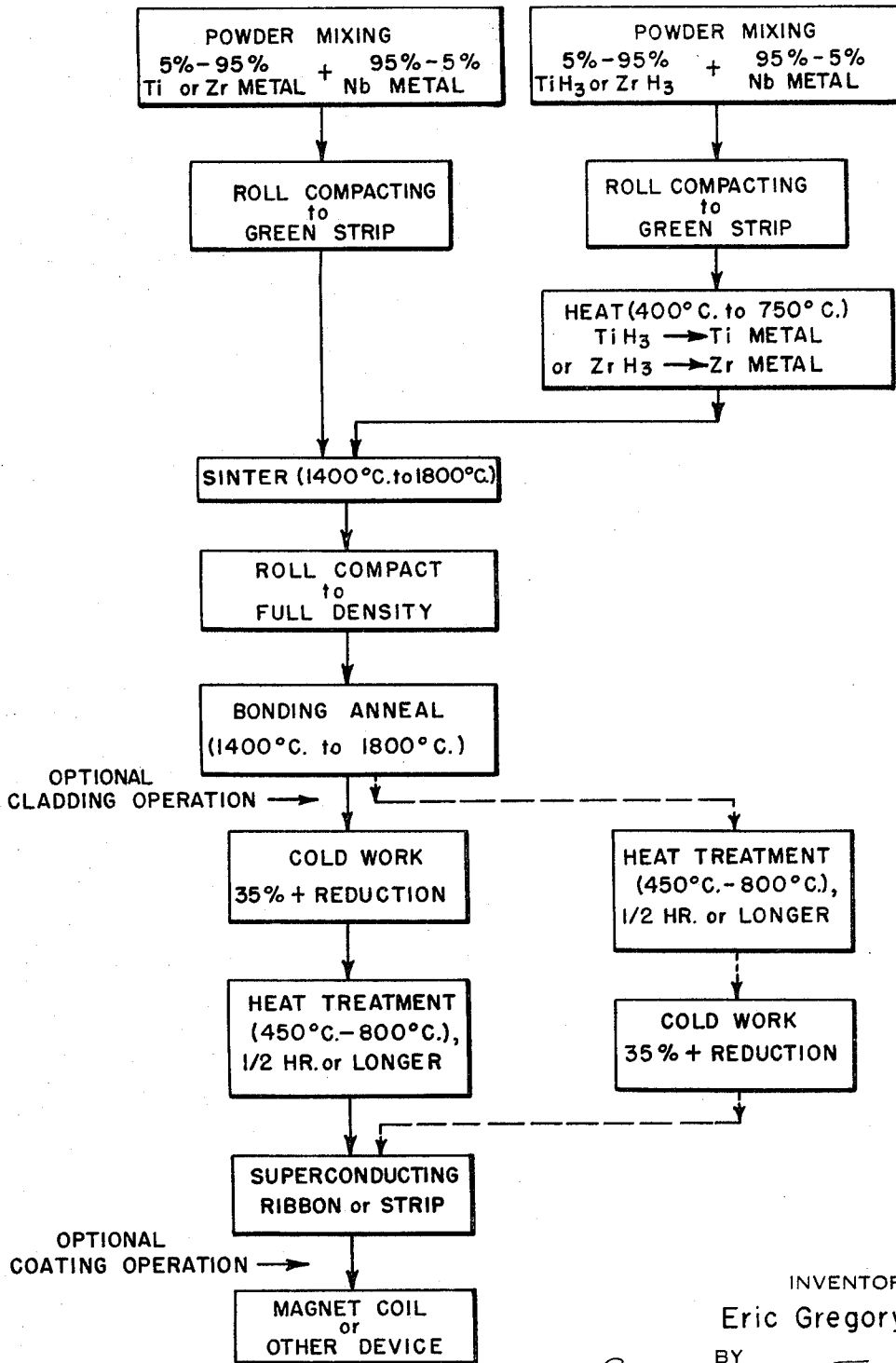
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FABRICATION OF NIOBIUM SUPERCONDUCTOR ALLOYS

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**FABRICATION OF NIOBIUM SUPERCONDUCTOR ALLOYS**

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15 Claims

**ABSTRACT OF THE DISCLOSURE**

A method is described for making niobium-titanium or niobium-zirconium superconducting strip by compacting a mixture of finely divided niobium and finely divided titanium or zirconium, sintering the green compact, rolling the sintered product to substantially full density, heating the fully dense strip at 1400° C. to 1800° C., cold working the resulting strip to a reduction of at least 35% in cross-sectional area, and then heat treating the cold worked product at a temperature between 400° C. and 800° C. for at least 15 minutes. Titanium hydride or zirconium hydride powder may be used in place of the corresponding finely divided metal, in which case the green compact is heated at 400° C. to 750° C. to decompose the hydride to metal before sintering at 1400° C. to 1800° C. All heating operations are carried out in an inert gas atmosphere, preferably in helium or, alternatively, in a vacuum. The final cold working is advantageously to a reduction in cross section of 80% or more, and the final heat treatment is preferably at 500° C. to 600° C. for about one hour. In the case of some of the zirconium containing alloys, if it is desired to obtain the highest current carrying capacity at high fields, this final heat treatment can precede, rather than follow the cold working operation.

The invention relates to the fabrication of niobium-titanium and niobium-zirconium alloys, and has for its principal object the provision of an improved procedure for producing superconducting alloys of such compositions in elongated shapes by powder metallurgy methods.

Niobium-titanium and niobium-zirconium alloys are important members of the family of superconductors. Their fabrication, however, has been tedious because of the difficulty of producing relatively homogenous bars by melting and casting. Conventional practice heretofore has involved repetitive casting and remelting of the metal, sometimes upwards of a dozen times, before producing a final cast bar suitable for rolling or drawing into wire or ribbon for use as a superconductor.

The present invention greatly simplifies the fabrication of niobium-titanium and niobium-zirconium alloys into elongated superconducting shapes (e.g., strip or ribbon), by eliminating the repetitive melting, casting, and remelting of prior practice. In accordance with the method of the invention, an elongated shape of niobium-titanium or niobium-zirconium alloy is prepared by compacting (preferably by direct rolling) of a mixture of niobium powder with titanium or zirconium powder (or with powdered hydride of titanium or zirconium) and then processing the compact of mixed powders by rolling or equivalent means into a finished superconductor strip, ribbon, or wire. The method of the invention involves mixing together finely divided metallic niobium with a finely divided Group IV material of the group consisting of metallic titanium, metallic zirconium, titanium hydride and zirconium hydride in the proportions of 5% to 95% by weight niobium and the balance the Group IV material. This mixture of powders is directly rolled or otherwise compacted to form an elongated cohesive green strip. The green strip is heated in an inert environment (either an

inert gas atmosphere or a vacuum) to an elevated temperature, initially above 400° C. and ultimately above 1400° C. but below 1800° C. to form a sintered metallic niobium alloy strip of increased physical strength. The sintered strip is compacted by rolling (or otherwise) until its density is increased to substantially the full density of the niobium alloy. The resulting full density strip is then heated in inert environment at a temperature in the range from 1400° C. to 1800° C. to insure bonding together and interdiffusion of all elements of the strip. Thereafter, the strip is cold-worked at least 35% reduction in cross-section (preferably upwards of 80% reduction in cross-section) and is subjected to heat treatment in an inert environment at a temperature in the range from 400° C. to 800° C. for at least 15 minutes.

When processing certain of the zirconium alloys, it has been found advantageous to give the final (400° C.—800° C.) heat treatment prior to the cold working treatment rather than after it.

The resulting cold worked and heat-treated alloy is in a desirable superconducting condition and may be used directly for winding magnet coils and for other uses as a superconductor. It may, however, be advantageous to coat the material at this stage with a normal conductor of low resistivity (such as copper or silver) before using it as a magnet winding. If a thick cladding of normal conductor is required, this cladding operation may be performed prior to the final cold working.

When finely divided titanium or zirconium hydride is used as a Group IV material in preparing the initial powder mix, the green compact prepared therefrom is first held at a temperature in the range from 400° C. to 750° C. for a short period of time (usually 5 to 15 minutes) to decompose the hydride to metallic titanium or zirconium, and is then heated to the higher sintering temperature in the range from 1400° C. to 1800° C. if, however, finely divided metallic titanium or zirconium is employed in preparing the powder mix, the green compact made therefrom may be heated without delay through the 400° C. to 750° C. range directly to the sintering temperature, for in such case, there is no need to hold the compact in the lower of these temperature ranges to form the fully metallic composition.

The proportions in which the niobium and Group IV material are mixed are not particularly critical, for superconducting alloys may be prepared over the entire broad range of compositions indicated above. However, it is generally customary to make compositions such as the following:

Niobium wet. percent:	Titanium or zirconium
60	40 wt. percent Ti
40	60 wt. percent Ti
75	25 wt. percent Zn
66	33 wt. percent Zn

Hence, a preferred range of concentration is approximately 40% to 75% by weight niobium and the balance, approximately 25% to 60% by weight, the Group IV material.

The inert environment in which all heating operations are carried out is either an inert gas atmosphere or a vacuum. The preferred inert gas is helium, although other gases which are non-reactive with the alloy may be employed successfully. Gases such as nitrogen, which are normally regarded as inert in many metallurgical operations, are not inert chemically with respect to niobium-titanium and niobium-zirconium alloys and, accordingly, are not satisfactory.

The invention is described in greater detail below with reference to the accompanying drawing, the single figure of which is a flow sheet showing the successive steps of the process of this invention.

Generally, I prefer to prepare the initial powder mix

by mixing together 5% to 95% by weight of fine divided metallic titanium or zirconium and the balance (95% to 5% by weight) of finely divided niobium metal. Preferably at least 90% of the particles of each component of the mix is in the size range between plus 200-mesh and minus 100-mesh, U.S. Standard Screen Series. The surfaces of the finely divided metallic particles are generally oxidized, and the amount of oxygen introduced into the superconductor alloy therefore, increases as the powder particles diminish in size. Some oxygen is desirable (if not absolutely essential for optimum properties) in the final superconductor, and an effective amount of oxygen appears to be introduced when the powder particles are of the screen analysis stated above. The total oxygen content in the powder is of course the important parameter, and this is dependent on the purities of the powders employed as well as on their particle sizes.

In lieu of finely divided metallic titanium or zirconium, a satisfactory powder mixture may be prepared using finely divided titanium hydride or zirconium hydride as the Group IV material. The screen analysis of this material should be about the same as that of the metal powder. Even these hydrides become contaminated with oxygen of the air, especially when subjected to the crushing action of the compacting rolls. Despite the hydrogen present in the hydride, oxygen evidently combines with titanium and niobium in the alloy prepared from such mixtures and is carried through into the final product.

In either case, after the powder mixture has been well blended by tumbling or otherwise, it is compacted into a green strip, preferably direct rolling utilizing conventional powder rolling technology. Other compacting means such as pressing in a die may be used, though such means impose a limit on the length of the final product which is not imposed by the roll compacting process. The compacted green strip should be as thick as possible, so that it may subsequently be subjected to severe cold working without reducing it to undesirable thinness.

If the green compact has been prepared from a mixture of titanium or zirconium hydride and niobium metal powders, it is heated to a temperature in the range from 400° C. to 750° C. and is held at such temperature for a period preferably in the range from 5 to 15 minutes, to effect decomposition of the hydride to metallic titanium or zirconium. It is then heated to a sintering temperature in the range from 1400° C. to 1800° C. and is held at such temperature for a further short period of time, which may be as short as one minute but which can, without disadvantage, be for as long as two or three hours or even more.

In cases where the green compact has been prepared directly from a mixture of titanium metal powder and niobium metal powder, it may be heated through the 400° C. to 750° C. temperature range without delay directly to the sintering temperature, for in this case there is no need to allow for thermal decomposition of a component of the compact.

Because of the sensitivity of the alloy to oxidation and to contamination by other elements, notably nitrogen of the atmosphere, it is necessary that the sintering operation (and the preceding thermal decomposition of the hydride, if needed) be carried out in an inert gas atmosphere or a vacuum. Helium is a particularly suitable inert gas in which to conduct these and all other heating operations involved in the process, for it is completely inert with respect to the alloy at the temperatures involved. Other noble gases such as argon and neon may also be employed successfully. The hydride decomposition step (when used) and the sintering operation can both be carried out in the same furnace in a batch type operation, by simply adjusting the heating rate and the time of heating at each particular temperature. These steps can also be carried out in separate furnaces, and this latter procedure has advantages where continuous processing of strip is employed.

The sintered compact is allowed to cool to room temperature in the inert gas atmosphere or vacuum and then is compacted to substantially the full density of the niobium alloy. Compacting advantageously is accomplished by rolling, but of course it can be accomplished by other means, such as by die compaction or by swaging. No appreciable cold work is performed on the alloy composition during compacting, but substantially all voids that are present in the sintered product are eliminated.

Before the compacted full-density strip can be cold worked, it must be subjected to a bonding anneal, in the course of which it is heated (again in an inert atmosphere or vacuum) to a temperature in the range from 1400° C. to 1800° C. During this operation the particles making up the compacted strip are bonded together by interdiffusion, and thereby the strip acquires sufficient physical strength to withstand intensive cold working. The time required for bonding to occur during the bonding anneal is not long. Three to ten minutes at a temperature between 1400° C. and 1800° C. is generally sufficient, although a longer period of heating is permissible. Although this heating operation is termed an "anneal," it is not its purpose to effect any substantial grain growth or homogenization of the alloy. Indeed, complete homogenization may not yield a superconductor with the most desirable properties.

At the conclusion of the bonding anneal, the strip is again allowed to cool to room temperature in the inert gas atmosphere or vacuum and then is subjected to cold working, most conveniently by rolling but by any other means desired. It is important that the degree of cold working be as great as possible. The strip should be cold worked at least to the extent of 35% reduction in cross-sectional area, and preferably it is cold worked to 80% or more reduction in area. The alloy, if it has not become excessively oxidized or otherwise contaminated, does not work harden significantly and is not subject to cracking or other failure during cold working, so no particular difficulty is encountered in thus severely working it. The most likely limitation on the degree to which it can be cold worked is the thickness of the strip at the beginning of cold working. It is difficult to roll a strip thinner than a half a mil (0.0005 inch), and for many purposes a final strip several mils in thickness is desired. The initial starting thickness must, of course, be great enough so that the desired degree of reduction in area can be achieved when the strip has been reduced to the desired final thickness. In those instances where initial thickness and other conditions permit, cold working to the extent of 99% and even more reduction in area is possible with these alloys, and is desirable in order to obtain optimum superconducting properties.

After cold working (preferably to final size) the strip is given a final heat treatment at a temperature in the range from 400° C. to 800° C., again in vacuum or in an inert gas atmosphere. The time of heating is longer at the lower temperatures within this range than at the higher temperatures. For example, if heating is in the range from 500° C. to 600° C., a treatment time at this temperature of at least about an hour is required. If heat treatment is in the range from 600° C. to 700° C., one-half hour is a sufficient treatment time.

The heat treatment of the cold worked metal produces a change in the alloy which greatly improves its superconducting quality by increasing its critical current density. However, the nature of the change that occurs upon heat treatment is obscure, and no doubt varies with the exact composition of the alloy. It appears that a precipitation of a separate phase takes place during the heat treatment and that this precipitated phase is more intimately dispersed through the alloy the more severe has been the preceding cold working. The nature of such precipitation is not known, however; and it is not even certain that the heat treatment results in the formation of a precipitated phase in some of the compositions.

Generally, especially with the niobium-titanium alloys, the severe cold working precedes the final heat treatment, as described. In the case of certain niobium-zirconium compositions, however, it has been found that it is sometimes advantageous to reverse the order of this operation, that is, to perform the 400°–800° C. heat treatment before the final cold working treatment.

The cold worked and heat treated product is the final fabricated superconductor. If in strip form, it may, of course, be slit to ribbon of any desired width. It may also be subjected to some further cold working, if it is desired to form it into some different shape. It is often desirable to coat the superconductor with a layer of a good normal conductor (e.g., copper, aluminum or silver); and this may be done by electroplating, roll bonding, or other conventional operation at this stage. If the superconductor is to be used in a large magnet, a thick layer of a normal low resistivity conductor may be required; and in such cases it may be desirable to clad the superconductor before the final cold rolling and heat treatment steps.

It is often desirable, for magnet applications, to make conductor assemblies comprising multiple strands of superconductor embedded in a normal conductor. The above-described procedures and variation of them may be used to make such assemblies in which the superconducting strands are produced by the method of this invention.

#### Example I

Titanium metal powder and niobium metal powder, each +200 mesh and –100 mesh, were blended in a laboratory blender in the proportions of 40% by weight of the titanium and 60% by weight of the niobium powder. The blended powders were compacted in a die at a pressure of 100,000 lbs. per square inch into a strip 6 inches long,  $\frac{3}{8}$  inch wide and 0.040 inch thick. This green compact strip was sintered for one hour in a helium atmosphere at 1450° C. and then, after cooling to room temperature, was cold rolled to a thickness of 0.030 inch, at which thickness it had substantially the full density of the niobium-titanium alloy. The full-density strip was bond annealed for 5 minutes at 1600° C. in a helium atmosphere and again cooled to room temperature. The strip was then rolled to a thickness of 3.5 mils (a reduction in cross-sectional area of about 80%). The cold worked alloy was heated at about 550° C. for one hour, again in a helium atmosphere. The resulting heat treated strip was tested for superconductivity at 4.2° K. and was found to be capable of carrying a current of  $1.6 \times 10^5$  amperes per square centimeter at 40 kilogauss.

#### Example II

Titanium hydride powder (–170 mesh and +220 mesh) was blended with –325 mesh niobium metal powder in the ratio of 40% by weight of the titanium hydride powder and 60% by weight of the niobium metal powder. The blended powder then was compacted by direct rolling into a strip 0.012 inch thick in a small laboratory powder rolling mill. The rolled compact was heated at 500° C. for five minutes in order to decompose the titanium hydride, and then the temperature of the strip was raised to 1600° C. at which temperature the strip was sintered for five minutes. All heating operations were carried out in atmosphere of helium. The sintered strip was compacted by rolling to substantially the full density of the alloy, resulting in a reduction in thickness to about 0.008 inch. This strip was then subjected to bond annealing in a helium atmosphere for five minutes at a temperature of 1600° C., after which it was cooled in the helium atmosphere to room temperature. The strip then was rolled to 0.005 inch, a reduction in cross-sectional area of 37.5%. This cold-worked strip then was heat treated at 650° C. for 35 minutes in a helium atmosphere. The strip thus produced was tested for current carrying capacity at 4.2° K. and was found to be capable

of carrying  $2.3 \times 10^4$  amperes per square centimeter at 40 kilogauss.

#### EXAMPLE III

Zirconium metal powder and niobium metal powder each having a screen analysis of 90% plus 200-mesh and 100% minus 150-mesh are mixed in the proportions 25% by weight zirconium, 75% by weight niobium in a laboratory blender. The blended powders are compacted by rolling to form a cohesive green strip  $\frac{1}{2}$  inch wide and 0.025 inch thick. The green strip is sintered at 1550° C. for five minutes in a helium atmosphere and cooled in such atmosphere to room temperature. It is then compacted by rolling to a thickness of approximately 0.015 inch, to substantially the full density of the zirconium-niobium alloy. The resulting strip is bond annealed for ten minutes at 1500° C. in a helium atmosphere and cooled in such atmosphere again to room temperature. The strip is heat treated at 800° C. for 45 minutes in a helium atmosphere, and then rolled to a thickness of 3 mils (a reduction in cross sectional area of about 80%). Upon testing for superconductivity at 4.2° K., the resulting heat treated and cold worked strip is found to be capable of carrying a current of  $5 \times 10^4$  amperes per square centimeter at 40 kilogauss.

I claim:

1. The method of making an elongated niobium alloy superconductor shape which comprises mixing finely divided metallic niobium with a finely divided Group IV material of the group consisting of metallic titanium, metallic zirconium, titanium hydride and zirconium hydride in the proportions of 5% to 95% by weight of niobium and the balance the Group IV material, compacting such mixture to form an elongated cohesive green strip, heating the green strip in an inert environment to an elevated temperature initially above 400° C. and ultimately above 1400° C. but below 1800° C. to form a sintered metallic niobium alloy strip of increased physical strength, compacting the sintered strip until its density is increased to substantially the full density of the niobium alloy, heating the resulting full density strip in an inert environment at a temperature in the range from 1400° C. to 1800° C., and thereafter cold working the strip at least 35% reduction in cross section and heat treating it in an inert environment at a temperature in the range from 400° C. to 800° C. for at least fifteen minutes.

2. The method according to claim 1 in which approximately 40% to 75% by weight of finely divided niobium is mixed with approximately 25% to 60% by weight of finely divided Group IV material.

3. The method according to claim 1 in which the green strip is formed by direct rolling of the powder mixture.

4. The method according to claim 1, in which at least 90% of the finely divided niobium and of the finely divided Group IV material is plus 200-mesh and minus 100-mesh U.S. Standard Screen series.

5. The method according to claim 1, in which finely divided metallic niobium is mixed with finely divided metallic titanium, and the green strip compacted from such mixture is directly sintered at a temperature in the range from 1400° C. to 1800° C.

6. The method according to claim 5, in which the compacted green strip is sintered at a temperature of about 1600° C. for above five minutes.

7. The method according to claim 1, in which finely divided metallic niobium is mixed with finely divided titanium hydride, and the green strip compacted from such mixture is first heated at a temperature in the range from 400° C. to 750° C. to decompose the titanium hydride to metallic titanium and then is sintered at a temperature in the range from 1400° C. to 1800° C.

8. The method according to claim 7, in which the

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compacted green strip is sintered at a temperature of about 1450° C. for about 1 hour.

9. The method according to claim 1, in which the inert environment in which at least one of the heating operations is performed in a vacuum.

10. The method according to claim 1 in which the inert environment in which at least of the the heating operations is performed in an inert gas atmosphere.

11. The method according to claim 10, in which the inert gas is helium.

12. The method according to claim 1, in which the full-density strip after heating is cold worked at least 80% reduction in cross section.

13. The method according to claim 1, in which the cold worked strip is heat treated at a temperature in the range from 600° C. to 700° C. for about one-half hour.

14. The method according to claim 1 in which the

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cold working operation precedes the final heat treatment.

15. The method according to claim 1 in which the cold working operation follows the final heat treatment.

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