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METHOD OF MAKING WIRE OF SUPER-
CONDUCTIVE MATERIALS

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This invention relates to superconductive materials, and more particularly to the method of making wire of such materials.

The characteristic of zero electrical resistance at extremely high magnetic fields and current densities, is exhibited by many materials including binary alloys of columbium, zirconium, titanium, tantalum, vanadium, molybdenum and hafnium. On the other hand, binary alloys of these types are characteristically difficult to fabricate into usable form, and hence their commercial utilization heretofore has not been realized.

It is a principal object of the present invention to provide a method by which superconductive materials such as the binary alloys enumerated above, may be formed into wire exhibiting excellent superconductivity, high strength and ductility.

Another important object of this invention is the provision of a method by which the formation of wire of superconductive materials is accomplished substantially entirely by cold working, a factor which contributes materially in the development of maximum critical current densities.

A further important object of the present invention is the provision of a method by which the formation of superconductive wire is achieved economically and at a high rate of production.

The foregoing and other objects and advantages of this invention will appear from the following detailed description of the present invention.

In its broad concept, the present invention involves the mechanical cross sectional reduction of a casting of superconductive material, under metallurgically cold conditions and under an initial condition of such compressive constraint that sufficient initial grain elongation is achieved without surface grain separation, cracking, or other failure to permit further unconstrained cold working down to wire form.

The general method of this invention is as follows: A superconductive alloy, for example of columbium and zirconium, is cast in the shape of an elongated rod not exceeding about one and one-half inches in diameter and preferably about one inch in diameter. The casting may be heat treated, if desired, to homogenize the structure, although it is not necessary. The rod then is subjected to metallurgically cold mechanical working, while under compressive constraint, to reduce its cross section by at least about fifty percent and preferably about seventy-five percent.

Working may be effected by swaging, rolling, extrusion, or other suitable means. Metallurgically cold temperature is any temperature below that at which recrystallization of the alloy occurs, and its range depends upon the alloy being treated. In the present illustration any temperature below about 1800° F. is considered metallurgically cold. However, it is desirable to utilize temperatures as low as practicable, consistent with the capabilities of the working apparatus and with the characteristics of the alloy being treated.

If necessary, further reduction is continued, either under constraint or unconstrained, until the rod is reduced to a size acceptable for drawing by conventional wire drawing apparatus. Present wire drawing apparatus is operable upon rods having a diameter of about one half inch or less, preferably about one quarter inch.

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Constraint of the rod may be afforded by confining the rod in a sheath of steel, copper, columbium, or other metal or alloy which is more ductile and tougher than the superconductive alloy being treated.

Although the function of the constraining sheath is not completely understood, it is believed that the sheath is forced by the swaging, rolling or extrusion pressure into firm contact with the surface of the rod, creating a compressive stress upon the surface of the confined rod sufficient to prevent the surface of the rod from cracking or otherwise failing. That is to say, since surface grain separation or other surface failure can occur only by movement of the adjacent surface area, separation cannot occur since the constraining force of the sheath prevents such movement. Deformation thus proceeds properly in the longitudinal direction of the rod.

The enclosing sheath provides the additional advantage of protecting the surface of the alloy rod from oxidizing atmosphere. It also provides a lubrication effect which enhances the mechanical working operation.

Alternatively, but not preferably, constraint of the rod surface may be afforded by extrusion of the rod under metallurgically cold, and preferably minimum temperature condition, without sheathing. It is believed that the constraining force of the extrusion die against the surface of the minimum heated rod serves to prevent movement of the rod surface, in manner similar to the effect of the sheath.

To exemplify the method of the present invention, a superconductive alloy of columbium and zirconium, in atomic percentages of 75 and 25, respectively, was formed initially in the shape of an elongated cylindrical casting, for example about six inches in diameter. The casting was cut longitudinally to provide a number of square rods, preferably not greater than about one inch square, for facility of subsequent working. The rod then was turned to three quarter inch diameter cylindrical form, since in the present illustration it was desired to form round wire.

The round rod then was enclosed in a steel tube having a wall thickness of about one eighth inch, and subjected to the action of a swage at a temperature ranging from atmospheric to about 1450° F., to effect cross sectional reduction of the rod. A temperature of about 800° F. was found to provide the best swaging characteristics.

When swaging had reduced the rod to about 0.4" diameter, the sheath split and hence was removed. However, it was found that the rod then could be swaged cold, at substantially atmospheric temperature, down to below 1/4" diameter and then drawn to wires of 0.020" and 0.010" diameters without the development of surface grain separation, cracking or other failure. The resulting wires exhibit good strength and ductility, with zero electrical resistance at current densities exceeding 10⁴ amperes per square centimeter at 85K gauss and 10⁵ amperes per square centimeter at 50K gauss at 4° K. or lower.

In the present illustration when the cracked sheath was removed the surface of the rod was quite roughened. It was found that improved drawing characteristics are obtained when this roughened surface is removed, as by grinding, prior to cold drawing.

In the alternative, care may be taken to prevent severe cracking of the sheath by visual inspection to discover the start of such cracking. The sheath then is annealed at about 1450° F. for about fifteen minutes. If cracking develops during subsequent reduction, annealing may be repeated. Other sheathing materials resist fracture during swaging, and hence may be retained on the rod throughout the entire swaging operation if desired.

When extrusion is substituted for swaging, the alloy casting is extruded either bare or in a sheath, at a metal-

lurgically cold temperature of not more than about 1600° F. Minimum temperature is preferred, and this is governed in part by the capabilities of the extrusion apparatus.

Having drawn the wire to 0.010" diameter, it will be apparent that the initial 3/4" diameter cast rod has been subjected to greater than 99.9% reduction entirely by metallurgically cold working. The effect of this treatment is manifest in the exceptional superconductivity, strength and ductility of the wire.

In contrast, attempts to swage, or otherwise mechanically work the 3/4" unsheathed cast rod at temperatures ranging from atmospheric to about 1450° F., and attempts to extrude the unsheathed rod at normal extrusion temperature of about 2900° F., resulted in surface grain separations and cracking of such magnitude that further processing was not feasible.

It will be understood that optimum working temperatures and percentage reductions while constrained, will vary with the types of superconductive alloys and with various types of sheathing or working apparatus. However, it has been demonstrated herein that mechanical reduction must be accomplished initially under the constraining effect described for otherwise surface grain separation or other failure occurs to the extent that commercially acceptable wire cannot be formed.

It will be apparent that the ultimate shape of the wire may be round, as described, or in the form of flat ribbon, or any other cross sectional configuration desired.

The foregoing and other changes and modifications may be made without departing from the spirit of this invention and the scope of the appended claim.

Having now described my invention and the manner in which it may be used, what I claim as new and desire to secure by Letters Patent is:

The method of making wire of a superconductive alloy

consisting essentially of about 75 atomic percent columbium and about 25 atomic percent zirconium, comprising forming the alloy into an elongated casting, having a cross sectional diameter not substantially exceeding one inch, enclosing the casting in a sheath of metal capable of confining the casting under compressive constraint, mechanically reducing the cross section of the alloy at a temperature of about 800° F. and by at least about fifty percent while confining the alloy in the sheath for at least an initial portion of said reduction, removing the sheath, and cold drawing the reduced alloy to wire form.

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