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COMPOSITE SUPERCONDUCTING STRUCTURES

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ABSTRACT OF THE DISCLOSURE

Described and claimed are formed structures consisting essentially of (1) a metal and/or polymer matrix and (2) a superconductor material, in amount of 20-90% by volume of the structure, which is in discontinuous fiber form, has an electrical resistivity of 5-35 micro ohms at 25° C., and is a Group IV-B or V-B transition metal, a carbide and/or nitride thereof, or an intermetallic compound thereof. The electrical conductivity of the structure is greater than that of (1) or (2) alone at room temperature.

Field of the invention

This invention relates to new compositions useful as superconductors. More particularly, it relates to new compositions consisting essentially of fibrous superconductors dispersed in a binder matrix.

Background and details of the invention

The phenomenon of superconductivity is well known, and many metals, alloys, and intermetallic compounds exhibit this unusual physical property under the proper conditions. The particular physical form of the superconductor surprisingly has a very large effect on the overall efficiency of the material as a superconductor. (See, for instance, the copending application of Forshey and Ring, Serial No. 313,439, filed October 3, 1963, concerning the surprisingly outstanding superconducting behavior of the there-defined fibrous forms of niobium carbide and niobium nitride.)

The present invention is concerned with an as yet not completely understood phenomenon wherein it has been observed that a combination of any one of several (including mixed) fibrous superconductors embedded, encased or placed in a binding or binder matrix results in an overall fiber/binder combination which is superconducting. The most surprising aspect of this invention is that irrespective of whether or not the binding or binder matrix itself is a superconductor, the combination of the fibrous superconducting material and the binding or binder matrix is overall a superconducting composition. Thus, the combination of the necessary superconducting fiber and the binding or binder matrix (which may or may not be a superconductor per se, and actually whether or not it is has no gross effect on the properties of the combination) results in a composite object with superconducting properties, i.e., higher conductivity, greater than the binder and greater than those of said matrix alone and said superconductor alone, both the latter two being in bulk form and all three being measured at equal cross section at the same temperature.

The composite of this invention is more readily handleable into shaped objects than the superconductor alone in either bulk or fibrous form. The matrix provides ductility, strength, and superconducting bridges from fiber to fiber. This latter point permits approximate realization of fine fiber superconductive properties without the necessity of long continuous individual fibers. Further, the common defect of known type II superconductors, namely brittleness, is not found in the composition of this invention.

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The fibrous superconductors which are useful in forming the just-described combinations of the present invention can vary widely and include NbC and NbN (as per the above-cited application of Forshey and Ring), TiN, Nb₃Sn, V₃Si, Zr/Nb, ZrN, V₃Ga, and fibrous Group IV-B and V-B metals, metal carbides and nitrides (including mixed metal carbides and nitrides), intermetallic compounds, and the like.

The binder or binding material which, together with the just-described superconducting fibers, forms the new superconducting composites of the present invention can vary widely and, as previously indicated, can be either a superconductor or a nonsuperconductor. Generally speaking, it will be a formable metal or polymer or mixtures thereof. The preferred binder matrices are the ductile nonferromagnetic metals. The ductility aspect is largely one of increased convenience and importance in that the composite fibrous superconductor/matrix material in those instances where the binder is ductile will be more readily formable as a composite into the desired shapes, e.g., wires, rods, bars, and the like.

Suitable specific matrix materials include metals, such as Pb, Sn, Mg, Al, Cu, Ag, Zn, etc., among the more easily handled metals. Others such as Ti, Nb, etc., which are much more refractory but which can be handled by powder metallurgy forming at comparatively low pressures, are also candidates. Possible forming techniques include extrusion, swaging, etc. As is true of the just-described and exemplary illustrated metal matrix materials, the polymeric matrix materials can also vary widely. Broadening speaking, the polymeric matrix material can be anything which is properly formable under conditions within which the superconducting fibrous filler material retains its superconductivity. Thus, the usable polymeric binder or matrix materials will generally include most of the deformable plastic polymers inclusive of the addition polymers, the condensation polymers, and the modified natural polymers. These classes include vinyl and vinylidene polymers, condensation polyesters, polyamides, and polyester amides, and ester amide and modified, e.g., esterified, etherified, cyanoethylated, etc., natural polymers.

Suitable specific examples of these various types include modified natural polymers such as cellulose acetate, cellulose acetate propionate, etc.; addition polymers and copolymers such as polyvinyl chloride/polyvinyl acetate copolymers, polyvinylidene chloride/vinyl acetate copolymers, polyethylene, fluorinated vinyl polymers such as polytetrafluoroethylene/hexafluoropropene copolymers and the like; condensation polyamides such as polycaprolactam, polyhexamethylenedipamide, polycaprolactam/polyhexamethylenedipamide / polyhexamethylenesecbacamide, and the like; condensation polyesters such as polyethylene terephthalate, polyhexamethylene terephthalate, poly[polytetramethylene glycol ether terephthalate], and the like; and condensation polyamide/polyesters such as polyhexamethylenedipamide/polyhexamethylene glycol terephthalate, polyhexamethylenedipamide/polyethylene glycol sebacate, and the like.

Thus, in the light of the foregoing specific illustrations and detailed exemplary disclosure which follows, it is apparent that the compositions of the present invention are formed structures or shaped composite objects consisting essentially of a dispersion or suspension of a superconducting fibrous material in a formable matrix, said matrix including polymers and ductile metals, both superconducting and nonsuperconducting such metals, and also being expressly inclusive of mixtures of said metals, and said dispersed or suspended fibrous material, which constitutes from 20% to 90% by volume (preferably greater than 50%) of said shaped object, is in discontinuous

fibrous form, has an electrical resistivity of from 5–350 micro ohm cms. at room temperature, and is selected from the class consisting of superconducting transition metals, metal carbides and nitrides (including mixed), intermetallic compounds, etc. The preferred fibrous materials are the superconducting nitrides and carbides of the elements of Group V–B. The electrical conductivity in a magnetic field of the said shaped object in the superconducting state is substantially greater than the conductivity of the said matrix similarly measured. The said composite shaped objects, i.e., the matrix material, preferably ductile metal, and the therein dispersed fibrous superconductor, as an overall unit preferably exhibit an I_c of $>10^4$ amps./cm.² at a field of $H>10$ oersteds.

The following examples, in which the parts given are by weight, are submitted to illustrate the present invention further but not to limit it. The fibrous superconductor component of the mixture of the present invention can be prepared in many ways. Illustrative of these fibrous materials and the manner in which they are prepared, the following examples show some of the permitted variations.

EXAMPLE I

Two alumina boats (4" x 1/2" x 1/2") were each charged with 5 g. of carbon black beads (25 mesh and smaller) and placed end to end in the center of a 36-inch long 1 1/2" O.D. x 1 1/4" I.D. commercial sillimanite (a 1/1 alumina/silica) refractory reaction tube. The tube and its contents were heated to 1425° C. for 16 hours, during which time 6 g. of niobium pentachloride was slowly sublimed into the reaction tube in a stream of nitrogen flowing at a rate of about 25 cc./minute. At the conclusion of the run, the upstream alumina boat contained a deposit of fine needles and small plates exhibiting a yellow metallic luster. X-ray analysis of this needle product showed it to be very pure niobium carbide with a cell constant of 4.470 versus values of

$$4.4702-4.4704 \pm 0.0005$$

as reported by Storms and Krikorian, J. Phys. Chem. 63, 1747 (1959). The fibrous niobium carbide exhibited a superconducting critical temperature of 17° K., a critical field (H_c) of well above 20,000 oersteds, and a rate of change of field strength with superconduction temperature (dH/dT_s) of approximately 9,000 oersteds/° K.

EXAMPLE II

Example I was substantially repeated except that the reaction temperature was 1360–1385° C., the reaction time was 7.5 hours, and 7.9 g. of niobium pentachloride was sublimed into the reaction zone over the reaction period using a 1:1 nitrogen/argon gas mixture flowing at the rate of 36 cc./minute. The upstream boat contained a deposit of both needles and plates of mixed niobium carbide/niobium nitride, i.e., single crystals of the mixed phases. X-ray analysis indicated the fibrous mixed crystals to exhibit a cell constant of 4.4464. Analysis of the mixed single crystals showed a 0.96% nitrogen content which corresponds to a mixed crystal containing 92.7% niobium carbide and 7.3% niobium nitride. The superconduction critical temperature of the fibers of the mixed crystals was 13° K. The downstream boat from the same synthesis contained a mixture of fibers and needles of niobium carbide/niobium nitride mixed crystals exhibiting an X-ray cell constant of 4.4583.

EXAMPLE III

An empty alumina boat of the type described in Example I was placed in a sillimanite refractory tube, also of the type described in Example I. The reactor was fitted with a concentric quartz tube which extended from the cold end of the reactor to the center of the hot zone. The assembly was heated to 1350° C. (internal temperature) for three hours, during which time 7.6 parts of niobium pentachloride was sublimed into the reaction zone

through the quartz inlet tube using a 40 cc./minute stream of dry nitrogen as a carrier. Simultaneously, hydrogen at the rate of 70 cc./minute was passed into the reactor through the annular space between the quartz tube and the sillimanite refractory tube. A light tan deposit of niobium nitride was obtained on the inside space of the quartz tube in the center of the furnace and niobium nitride rosettes in the form of short, very fine niobium nitride fibers were obtained at the bottom of the alumina boat. A sample of this product from a similar run on X-ray analysis was shown to be niobium nitride with a cell constant of 4.388. This material exhibited a superconduction critical temperature of 15° K.

EXAMPLE IV

An alumina boat (4" x 1/2" x 1/2") was charged with 10 g. of silicon and placed in the center of a 36 inch long 1 1/2" O.D. x 1 1/4" I.D. commercial sillimanite refractory reaction tube. The tube and its contents were heated to 1475° C. for 23 hours, during which time 7.8 g. of $TiCl_4$ was passed into the reaction tube in a stream of nitrogen flowing at a rate of about 45 cc./minute. At the conclusion of the run fine, fibrous TiN was obtained as a deposit on the upstream end of the alumina boat and on the tube walls around the upstream end of the boat. This product was extracted with 48% HF; 1.02 g. of HF-extracted fibrous TiN was obtained, exhibiting a T_c of about 5.6° K.

EXAMPLE V

The individual fibers of a sample of fibrous titanium nitride as per Example IV were manually separated and stranded into a thread. The individual fibers involved were up to 1/2–3/4" in length and from 2–10 microns in diameter. The resulting thread was approximately 1 1/4" long and over 100 microns in diameter. Electrical leads were attached to this thread using an air-driable silver paint. The leads were so arranged with respect to the thread that the resistance of the silver paint/thread contacts was in series with the resistance of the TiN thread and a small residual resistance was measured below the transition. The resistance R (at 4.2° K. which changes with current) was obtained and ratios of this resistance R/R_N , where R_N is the normal state resistance, were calculated. The following results were obtained where the ratio R/R_N has been multiplied by 100 and is expressed as a percentage of the normal resistance.

I, A.:	R/R_N (percent)
6×10^{-5} -----	5
1×10^{-3} -----	25
1×10^{-2} -----	70
3×10^{-2} -----	1 ~ 100

¹ No transition.

The above thread was then subjected to vapor deposition of metallic tin until an approximately 100 A. coating was obtained. The electrical properties of the coated thread were then determined as before at 4.2° K. measuring the electrical resistance as a function of the sample current. In this determination, the electrical leads were attached to the coated thread so that the silver paint/thread contact resistance was not measured and only the specimen resistance, including the individual fiber and fiber/fiber contact resistances, was measured. The results are as follows:

I, A.:	R/R_N (percent)
2×10^{-4} -----	2
1×10^{-3} -----	10
1×10^{-2} -----	40
3×10^{-2} -----	80

The tin-plated TiN thread just described was again subjected to tin metal deposition until an approximately additional 100 A. coating was deposited, thereby leaving the TiN thread with an approximate 200 A. coating of metallic tin. The electrical properties of this doubly coated

TiN/tin thread composite were determined as described above with the following results:

I, A.:	R/R_N (percent)
4×10^{-5} -----	<.01
6×10^{-5} -----	0.23
1×10^{-4} -----	2.3
2×10^{-4} -----	5.5
5×10^{-4} -----	14
1×10^{-3} -----	16
5×10^{-3} -----	26
1×10^{-2} -----	37
2×10^{-2} -----	64
4×10^{-2} -----	94
6×10^{-2} -----	99

A second thread of TiN fibers, treated as above to obtain an approximate 200 A. coating of metallic tin, was electroplated to provide an additional layer of metallic tin using a 1% stannous sulfate solution, a bulk metallic tin anode, and the fiber bundle as the cathode while passing 0.1 milliamperes of current for five minutes. The additional metallic tin coating was spongy in character and exhibited relatively poor adherence to the fiber bundle. The electrical properties of the thus obtained vapor-coated and electrically coated TiN/tin composite were determined using the previously described techniques with the following results:

I, A.:	R/R_N (percent)
2.5×10^{-6} -----	0.14
5×10^{-6} -----	0.61
1×10^{-5} -----	1.4
1×10^{-4} -----	3.6
5×10^{-4} -----	7.3
1×10^{-3} -----	60
1×10^{-2} -----	¹ 100

¹ No transition.

As a further control, another TiN thread was prepared, essentially as described in the foregoing, and the electrical properties thereof determined with the following results:

I, A.:	R/R_N (percent)
5×10^{-6} -----	$<6 \times 10^{-3}$
3.5×10^{-5} -----	$<6 \times 10^{-3}$
6×10^{-5} -----	0.31
1×10^{-4} -----	2.7
1×10^{-3} -----	20
5×10^{-3} -----	52
1×10^{-2} -----	79
3×10^{-2} -----	¹ 100

¹ No transition.

Other data with varying fields are:

Field (oersteds):	Critical temperature of composite, ° K.
0 -----	5.45
200 -----	5.15
400 -----	4.90
600 -----	4.65
800 -----	4.3

The above experiments show that when a superconducting fibrous material is embedded, dispersed, or suspended in a binder or binding matrix material, which may be but does not have to be per se superconducting, the composite structure is overall superconducting and readily handleable to form shaped objects of any desired structure. For example, when a TiN thread is coated by vapor-depositing Sn on the fibers, the amount of current re-

quired to produce a given R/R_N is increased above that of the untreated thread as shown in the following table:

I, Amps	R/R_N (Percent)		
	No Sn	Heavy Sn	Light Sn
6×10^{-5}	0.3	0.23	-----
1×10^{-4}	2.7	2.3	-----
2×10^{-4}	8.9	5.5	2.0
1×10^{-3}	20	16	10
1×10^{-2}	79	37	40
3×10^{-2}	100	94	80

EXAMPLE VI

TiN fibers coated with 1000 A. Cu were fabricated into "threads," and were examined for superconductivity through electrical resistance measurements. The four-probe technique was used and contacts were formed with silver paint.

The structure composed of TiN/Cu fibers exhibited a room temperature resistance of ~ 20 ohms. At 4.2° K. and at a low currents ($\sim 20 \mu\text{A.}$) superconductivity¹ was observed in this specimen. The transition to the normal state was caused by either increasing the temperature or the current density and a normal resistance, R_N , of 30 ohms was measured. The fact that this value is larger than the room temperature resistance of the thread is probably due to fiber-fiber contact resistances which can vary with temperature due to thermal contraction of the fibers.

The data obtained at 4.2° K. are given below.

I, Amps:	R/R_N (percent)
3.0×10^{-2} -----	100
3.6×10^{-3} -----	50
1.1×10^{-4} -----	10
8×10^{-5} -----	1
5×10^{-5} -----	<0.1

EXAMPLE VII

A mixture of 0.3 part of TiN fibers as per Example IV and 0.3 part of a 15% by weight solution of cellulose acetate in acetone was mixed with additional acetone to afford a readily spreadable consistency and then spread on a polyethylene terephthalate film. The acetone was allowed to evaporate from the thus spread film. During drying, the coating of the cellulose acetate/TiN composition lifted from the polyethylene terephthalate backing, and the thus obtained composite film at 4.2° K. exhibited a definite transition as the measuring current was increased above a critical value. The critical current density was 1.85 amps/cm.².

Another sample of the same cellulose acetate/TiN fibers/acetone composition was extruded through a conventional fiber-forming spinnerette with a 10-mil diameter opening. The resultant extrudate fiber, or wire, was allowed to dry at room temperature (i.e., the acetone was evaporated) thereby resulting in an approximate 60/40 by volume TiN/cellulose acetate wire. Microscopic examination showed that the TiN fibers were very well aligned along the primary wire axis, i.e., the length. The dried wire showed a definite transition as the measuring current was increased above a critical value as determined at 4.2° K. The critical current density was about 30 amps/cm.².

On an additional sample of the TiN/cellulose acetate composition, the resistance (R) as a function of the current through the specimen was measured at 4.2° K., as in the previous examples, with the following results wherein R_N is the resistance of the specimen in the normal state. In this particular sample of the TiN/cellulose acetate formulation, alignment of the fibers of TiN axially in the prime dimension of the fiber composite was not as evident as in the sample just previously described. Cur-

¹ Superconductivity, as defined here, is indicated by a decrease in resistance by at least a factor of 1000. Resistances smaller than $R_N/1000$ could not be measured due to the lack of sufficient sensitivity of the apparatus.

rent densities of 14–15 A./cm.² caused a measurable resistance and hence can be taken as the critical current density for this particular sample. A resistance change of about 10⁵ was observed in the transition to the normal state.

Current, A.:	R/R _N (percent)
30×10 ⁻² -----	100
17×10 ⁻² -----	50
7.0×10 ⁻³ -----	10
5.5×10 ⁻³ -----	5
3.6×10 ⁻³ -----	1
3.1×10 ⁻³ -----	0.5
2.5×10 ⁻³ -----	0.1
2.4×10 ⁻³ -----	0.05
2.1×10 ⁻³ -----	0.01
2.0×10 ⁻³ -----	0.005
1.7×10 ⁻³ -----	0.001

The fibrous superconductor components, for mechanical properties and coupled superior handling characteristics in the fabrication of elements and devices based on these fibrous materials, as well as for improved electrical behavior, preferably exhibit certain dimensional ratios, i.e., length to width of 50 to 10,000. The fibrous materials will range in fiber diameter from .01 micron to 20 microns and will normally be in the range 0.1 millimeter to 1 centimeter in length.

These new composite superconducting compositions are useful in the preparation of cryotrons, which preparations are well known in the art. More particularly, these composite products are useful in the formation of wire-wound cryotrons or thin film cryotrons and they are also useful in thin film form to produce both field-induced and current-induced transitions in such cryotrons. These cryotrons are operable as circuit components in the so-called binary adders, catalog memories, and tree and matrix circuits. The new composite products are also useful in preparing computer memory devices, particularly of the type known in the art as an inductively coupled cell or a Crowe cell. These products are useful further in the well-known superconducting field in the preparation of low-frequency and high-frequency devices, radiation detectors, and the like. They are also useful in the preparation of devices operating with either or both high currents and high fields. They are also useful in electromechanical applications, as is known for other superconductors, and in addition also exhibit the tunnel effect when suitably device-fabricated.

These composites exhibit very high current-carrying capabilities in high fields and are especially useful in such devices as superconducting magnets for general research purposes, massing action acceleration, plasma physics, and the like; superconducting transformers, rectifiers, tunnel diodes, and other like electrical devices; superconducting frictionless bearings for gyroscopes, motors, and the like; and similar other related device outlets.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. Formed structures consisting essentially of (1) a formable matrix selected from the class consisting of metals, polymers, and mixtures thereof, and (2) at least

one other material contained therein, said other material being further characterized as (a) comprising from 20 to 90 volume percent of said formed structure, (b) having a discontinuous fibrous form, (c) having an electrical resistivity of from 5 to 350 micro ohm cms. at room temperature, (d) being a superconductor and (e) being selected from the class consisting of niobium, titanium, vanadium and zirconium metals, the carbides thereof, the nitrides thereof, mixtures of said metal carbides and nitrides, and intermetallic compounds of said transition metals, with the electrical conductivity of said formed structure being substantially greater than the electrical conductivity of said matrix alone and said superconductor (2) alone, both in bulk form and all measured at equal cross section at the same temperature.

2. A shaped composite object consisting essentially of (1) a matrix consisting of a ductile non-ferromagnetic metal and (2) one other material dispersed therein, said other material being further characterized as (a) comprising from 50 to 90 volume percent of said composite object, (b) having a discontinuous fibrous form, (c) having an electrical resistivity of from 5 to 350 micro ohm cms. at room temperature, (d) being superconducting, and (e) being a carbide of niobium, titanium, vanadium or zirconium, with the electrical conductivity of said composite object being substantially greater than the electrical conductivity of said matrix alone and said superconductor (2) alone, both in bulk form and all measured at equal cross section at the same temperature.

3. A shaped composite object consisting essentially of (1) a matrix consisting of a ductile non-ferromagnetic metal and (2) one other material dispersed therein, said other material being further characterized as (a) comprising from 50 to 90 volume percent of said composite object, (b) having a discontinuous fiber form with the fibers thereof having a diameter in the range from 0.01 microns to 20 microns and a length in the range from 0.1 millimeter to 1 centimeter, (c) having an electrical resistivity of from 5 to 350 micro ohm cms. at room temperature, (d) being superconducting, and (e) being a nitride of niobium, titanium, vanadium or zirconium, with the electrical conductivity of said formed structure being substantially greater than the electrical conductivity of said matrix alone and said superconductor (2) alone, both in bulk form and all measured at equal cross section at the same temperature.

4. A composite object as defined in claim 2 wherein said other material is niobium carbide.

5. A composite object as defined in claim 3 wherein said other material is niobium nitride.

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