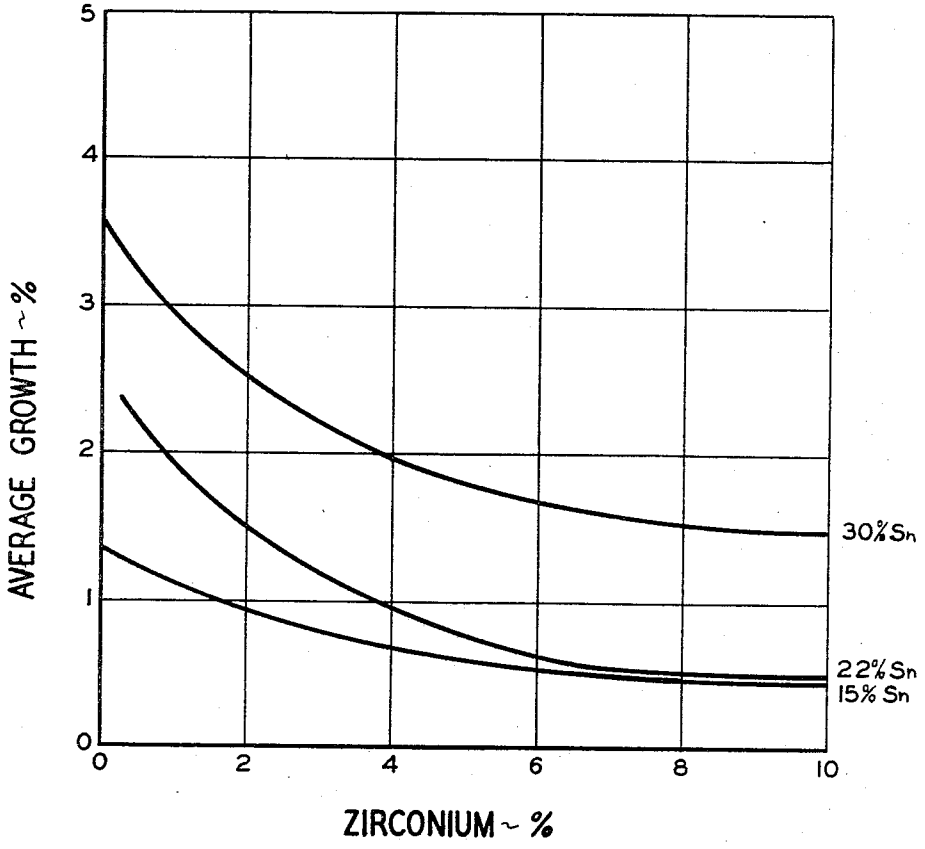
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METHOD FOR PRODUCING A SUPERCONDUCTING COATING
RESISTANT TO THERMAL GROWTH
Filed Jan. 11, 1968



MATERIALS HEAT TREATED 1-4
HRS. AT 1000°C

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METHOD FOR PRODUCING A SUPERCONDUCTING COATING RESISTANT TO THERMAL GROWTH

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U.S. Cl. 117—227 7 Claims

ABSTRACT OF THE DISCLOSURE

A method for producing a superconducting coating on a substrate which will be resistant to thermal growth upon heat treatment which comprises prereacting metallic particles of niobium or vanadium with an appropriate gettering material to form a powder, mixing the powder with appropriate particles of either tin, aluminum or silicon, feeding the mixture into a high thermal content plasma which is being directed against the substrate and heat treating the structure.

This invention relates to an improved method for producing a superconducting coating.

BACKGROUND

Superconducting materials which can maintain high current densities in high magnetic fields are in strong demand for fabricating high field superconducting magnets, magnetic field shields, energy storage cells, etc. Recent experimentation has established that certain compositions such as those of niobium-tin, niobium-aluminum, niobium-zirconium and vanadium-silicon yield high critical current densities. Current densities in excess of 10^5 amps/cm.^{2} in magnetic fields over 120 kilogauss have been achieved with niobium-tin alloys when in the desired superconducting phase Nb_3Sn.

A preferred process for fabricating any of the above mentioned compositions into a superconducting device is described in copending application Ser. No. 456,412 filed May 17, 1965 and now Pat. No. 3,407,049 in the name of D. C. Freeman et al. In accordance with such process elemental powdered metallic material is introduced into a high temperature gas stream to produce a high velocity stream of heated particles in the manner described in U.S. Pat. 3,016,447 and then projected against a suitable base to form a dense coating with an overlapping lamellar leaf structure of each element of material used. Subsequent heat treatment is thereafter essential for the coated alloy, especially niobium-tin, to form the desired superconducting phase into a continuous intermetallic network. The base upon which the coating is formed may if desired be removed depending upon the end use of the coating composition.

It has recently been discovered that during the heat treatment of niobium-tin, the material has a marked tendency toward thermal growth which upon cool-down is irreversible. This phenomenon is also attributable to other superconducting intermetallic compounds such as niobium aluminide and vanadium silicide. Measurements taken for the Nb_3Sn stoichiometric mixture show a linear dimensional increase of up to 4 percent. A dimensional increase of such magnitude causes gross distortion and cracking in the relatively weak Nb—Sn in applications such as superconductive solenoid windings thereby limiting the utility of the material to relatively simple structures.

OBJECTS

It is therefore, a primary object of the present invention to provide an improved method for producing a superconducting coating which resists thermal growth during heat treatment.

It is a further object of this invention to provide an improved method for forming a superconducting niobium-tin coating on a substrate which will resist thermal growth during heat treatment and which will yield a critical current density in excess of 10^4 amps/cm.^{2} in a magnetic field in excess of 120 kilogauss.

Other objects and advantages will become apparent from the following detailed description of the invention in connection with the accompanying drawing in which: the sole figure is a graph showing percent zirconium plotted vs. percent average thermal growth for different percentage compositions of niobium-tin.

SUMMARY OF INVENTION

In accordance with the present invention, a method is provided for producing a superconducting coating having a high critical current density which involves reacting metallic particles selected from the group consisting of niobium and vanadium with a gettering material to form a metallic powder, mixing said metallic powder with appropriate metallic particles selected from the group consisting of tin, aluminum and silicon; introducing said mixture into a high thermal content plasma to form a high velocity stream of heated particles, directing said stream of heated particles onto said substrate; and heat treating the resultant structure to form an intermetallic compound intermixed in interlocking relationship with said gettering material.

In accordance with the above process a superconducting coating composition is produced the preferred embodiment of which consists essentially of the intermetallic compound Nb_3Sn, with the remainder zirconium in a range from 1 to 10% by weight with 5% by weight being optimum.

As hereinbefore mentioned, compositions formed from niobium-tin, niobium aluminum and vanadium silicon possess superior superconducting properties for certain high field magnetic applications requiring a high critical current density. Such materials, however, have a marked tendency toward thermal growth during heat treatment. A detailed examination of photomicrographs of coated niobium-tin specimens heat-treated at different temperatures showed evidence of porosity which did not seem to be related to the coated niobium-tin specimens prior to heat treatment. More significantly, this porosity was not apparent until temperatures greater than 700–800° C. had been reached. At such temperatures the dimensional increase for stoichiometric Nb_3Sn due to thermal growth was substantial. During heat treatment in a vacuum, a rise in pressure over the niobium-tin material was also observed at about this temperature. Efforts to analyze the gas produced at these temperatures show that the gas which evolved from the base upon which the coating was formed was more detectable than that from the Nb—Sn material at the same analytical sensitivity. Thus if there was any gas being liberated by the Nb—Sn it was being trapped.

On the basis of such observations it can be theorized that thermal growth is a result of the liberation of gas metallurgically contained in the as plated NB—Sn material so as to form voids, many of which are prevented from "healing" by retention or trapping of the gas. The liberation of gas is expected because of the low solubility of oxygen and probably carbon in the niobium-tin compounds formed during heat treatment. Trapping of gas is believed to occur because of the fact that most of the

initial porosity is eliminated by capillarity at the melting point of tin, and furthermore, at temperatures above about 690° C. all niobium-tin compounds are apparently peritectoid so that any escape channels for escape of the gas must be created through solid material.

A number of coated niobium-tin samples were examined prior to heat treatment and found to contain .8–1% oxygen and .03% C. A simple calculation shows that if 1% oxygen is liberated within the Nb—Sn coated material at 700° C. and one atmosphere, then the sample volumes would almost triple. Actually the growth is not this drastic since some of the gas is chemically retained and some escapes completely.

Susceptibility to thermal growth is therefore believed to be directly attributable to the liberation of gas. Compositions of niobium and aluminum as well as vanadium and silcion have a propensity toward thermal growth similar to that of niobium and tin. The same conclusion can thus be drawn for coatings formed from these compositions.

Experimentation has established that the addition of at least one gettering material to the desired superconducting material reduces thermal growth. The gettering material acts to chemically retain the gases in the material. The more compatible the gettering material is to the gases being evolved the greater the reduction in thermal growth.

For the preferred niobium-tin material, it has been shown that the evolved gases are principally oxygen and oxides of carbon. Therefore, the gettering material should be one having a high affinity for oxygen and oxides of carbon. There are a number of getter materials which may be employed for this purpose such as titanium, aluminum and zirconium. Zirconium, however, in addition to being an excellent gettering material enhances significantly the super-conducting characteristics of the composition and is therefore preferred over the others.

The single figure shows the effect of zirconium on thermal growth for various niobium-tin compositions. As is apparent from the graph thermal growth decreases as the percentage of zirconium added is increased. For the particular concentration of contained gases involved for the data of the graph, the effect becomes insignificant above approximately 6% zirconium. It is obvious that should higher levels of contained gases exist in the niobium-tin materials, then the effect of the getter material on the thermal growth would persist to higher getter concentrations. Since the amount of getter material "dilutes" the niobium-tin material and therefore results in a lower ultimate concentration of the desired superconducting phase, it is important to avoid the addition of more getter than is required to prevent excessive thermal growth. The preferred addition of zirconium in the niobium-tin compositions having .8–1% O_2 and .03% C is in the range of 1–10% by weight with 5% by weight being optimum.

It was first believed that zirconium powder in the appropriate amount could be added to elemental powders of niobium-tin to form a coating of superconducting material by means of an arc torch as taught in the aforementioned copending application Ser. No. 456,412. However, it was found that merely mixing the powders together and introducing them into an arc effluent did not produce a satisfactory coating. Moreover, thermal growth upon heat treatment was not being curtailed to the extent expected. When, however, the zirconium is prereacted with niobium to form a powdered niobium-zirconium alloyed material which is then mixed with metallic particles of tin and introduced into the arc torch a sound, dense uniform continuous coating is produced. The reason underlying the initial requirement for prealloying zirconium and niobium rather than merely mixing them together remains unclear.

The powdered-zirconium alloy is prepared by first blending niobium and zirconium, then sintering or reacting the blended powder and thereafter milling the product to the desired powder mesh size. The prereacted powdered alloy is then mixed with metallic particles of tin in the appropriate proportion and put through the arc torch to deposit a layer of superconducting material onto a suitable base which is thereafter heat treated. During heat treatment, thermal growth is inhibited in the 700–880° C. temperature range through the chemical reaction between the zirconium and the gases being evolved. The specific reactions that occur during heat treatment are very complex and not completely understood. One theoretical explanation is that as the tin diffuses into and reacts with niobium to form the intermetallic compound Nb_3Sn, the oxygen contained within the niobium in the absence of zirconium is liberated from solution as a gas while in the presence of zirconium the oxygen chemically reacts with the zirconium forming zirconium oxide which is sufficiently stable as to prevent the liberation of gas.

The preferred process for producing the superconducting coating on a suitable substrate is taught in copending application Ser. No. 456,412. As described therein an electric arc is struck between two electrodes into which a gas stream is passed to produce a high thermal content plasma. The prereacted niobium zirconium powder, intermixed with metallic particles of tin, is introduced into the plasma to heat and propel the powder onto the substrate. The substrate may be any material which is solid and chemically stable at applicable temperature. Since the post heat treatment occurs around 700–800° C. the substrate would have to be solid having a melting point higher than 800° C. Best results have been accomplished with a non-transferred electric arc torch of the type shown and described in U.S. Pat. No. 3,016,447. The orifice of the arc torch shown therein is constricted so as to cause an intense collimated arc plasma. The powdered metallic material introduced into the arc or starting feed material consists of about 60–89% by weight niobium and 1–10% by weight zirconium which is intermixed with 10–30% by weight tin wherein 85% by weight prereacted niobium zirconium intermixed with 15% by weight tin is optimum.

It is contemplated by the following claims to cover any modifications which fall within the true spirit and scope of this invention.

What is claimed is:

1. A method for producing a superconducting coating, selected from the group consisting of niobium-tin, vanadium silicide and nobium aluminide containing a gettering material, upon a substrate, said coating having a critical current density in excess of 10^4 amps/cm.^{2} and a critical magnetic field in excess of 120 kilogauss comprising the steps of: reacting metallic particles selected from the group consisting of niobium and vanadium with a gettering material to form a metallic powder, mixing said metallic powder with appropriate metallic particles selected from the group consisting of tin, aluminum and silicon; introducing said mixture into a high thermal content plasma to form a high velocity stream of heated particles, directing said stream of heated particles onto said substrate; and heat treating the resultant structure to form an intermetallic compound intermixed in interlocking relationship with said gettering material.

2. A method as defined in claim **1** wherein said gettering material is selected from the group consisting of zirconium, titanium and aluminum.

3. A method for producing a superconducting coating on a substrate, the coating having a critical current density in excess of 10^4 amps/cm.^{2} and a critical magnetic field in excess of 120 kilogauss, comprising the steps of: prereacting metallic particles consisting of niobium and zirconium to form a niobium-zirconium metallic powder; mixing said metallic powder with metallic particles of tin; introducing said mixture of particles into a high thermal content plasma to form a high velocity stream of heated particles, directing said stream of heated particles onto said substrate; and heat treating the resultant structure

to form the intermetallic compound Nb_3Sn intermixed in interlocking relationship with said zirconium.

4. A method for producing a superconducting coating having a critical current density in excess of 10^4 amps/cm.^{2} and a critical magnetic field in excess of 120 kilogauss, comprising the steps of: prereacting metallic particles consisting of niobium and zirconium to form a niobium zirconium metallic powder; mixing said powder with metallic particles of tin; introducing said mixture of particles into a high thermal high velocity arc effluent; directing said effluent onto a suitable base material to form a dense coating thereon; and heat treating the resulting structure to form the intermetallic compound Nb_3Sn and zirconium.

5. A method as defined in claim 4 wherein said niobium is prereacted with 1–10% zirconium.

6. A method as defined in claim 5 wherein said niobium is prereacted with 5% zirconium.

7. A coating powder to be introduced into an electric arc coating device to form a dense coating upon a suitable substrate which will be resistant to thermal growth upon heat treatment, said powder consisting essentially of prereacted metallic particles of niobium-zirconium consisting of about 60–89% by weight niobium, and 1–10% by weight zirconium intermixed with 10–30% by weight metallic particles of tin.

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