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ELECTRICAL SEMI-CONDUCTORS AND METHOD OF MANUFACTURE

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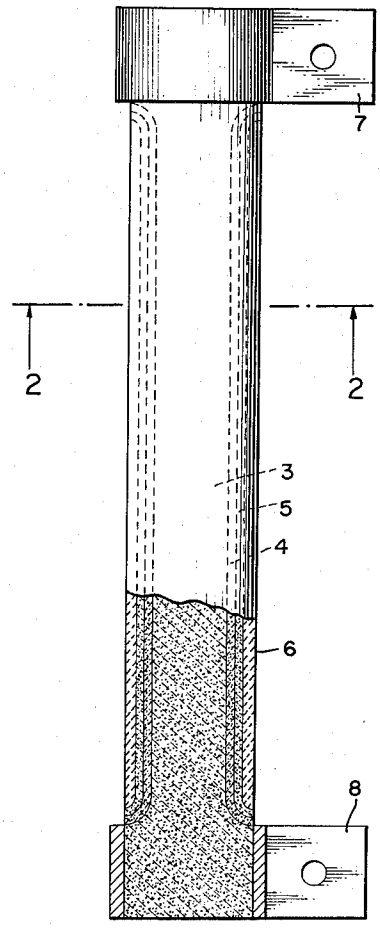
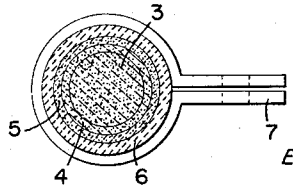


Fig. 1

Fig. 2



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ELECTRICAL SEMI-CONDUCTORS AND METHOD OF MANUFACTURE

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This invention relates to processes of manufacturing electrical semi-conductors and to electrical semi-conductors manufactured according to the invention.

An examination of the electrical resistance of the materials used in electrical engineering shows that there are many materials available which have a high electrical conductivity such as metals and also many materials which are useful as insulators such as metal oxides. Between the conducting materials on the other hand, there is a broad gap occupied by comparatively few materials. In practice, the carbides represent the only material which is of practical importance, the most important material being silicon carbide as material for electrical semi-conductors.

In the electrical industry, there is a substantial need for electrical semi-conductors as such conductors can be advantageously applied in various fields, for instance, as heating elements in industrial furnaces and electrical appliances, as conductors in electrical bulbs or as resistors for a variety of electrical devices. The industrial furnace industry particularly requires semi-conductors. Reference is made to this particular field of application to point out the deficiencies of the semi-conducting materials hitherto available. The principal commercially available materials are:

(1) Chromium—iron and aluminum alloys for temperatures up to 1300° C.
(2) Platinum for temperatures up to 1400° C.
(3) Silicon carbide for temperatures up to 1500° C.
(4) Molybdenum and tungsten for temperatures up to 2000° and 2500° C., respectively.
(5) Carbon and graphite for temperatures up to 3000° C.

The above enumerated materials have certain disadvantages which make the use of these materials in certain instances difficult or at least complicated. These disadvantages are primarily the following ones.

The conductors mentioned under Nos. 1, 2, 4 and 5 (carbon) have too low resistance values. Consequently, they cannot be operated with standard line voltages. As a result, transformers are frequently necessary that are more expensive than the furnaces proper. In many industrial furnaces it is necessary to protect the material to be annealed with a protective gas, frequently hydrogen. Hydrogen tends to corrode conductors No. 2 and 3 and also No. 5 (carbon) when higher temperatures are applied. No. 2 (platinum) being a precious metal is very expensive. The conductors of group 4 resist very high temperature, but can be heated only in the presence of protective gases since already at about 700° C. oxidation begins resulting in a destruction of the heating element. The previous discussion demonstrates some of the difficulties that are present in the design of industrial furnaces. There are missing particularly heating elements for temperatures up to about 1800° C. which can be operated in the presence of protective gases and also in air. Furthermore, such conductors should have a resistance value appreciably higher than metals so that they can be connected directly, that is, without transformers to standard line voltages. It will be apparent that materials for heating elements which stand up to the previously discussed high temperature requirements of industrial furnaces would be greatly desirable as they permit to operate the heating elements without intermediate steps at low loads and in cold condition.

The basic reason for the absence of suitable semi-conductors can be probably found in the large gap between the resistance values of metals and the resistance values of oxide insulators, the resistance values of the latter being higher by several decades.

Ceramics represent a material by means of which resistance values between the values of metals and of insulators can be achieved by sintering mixtures of metal powders and insulating oxide powders. However, the reduction of the electrical conductivity of the conductor—assuming powders are employed having conventional grain sizes—is controlled by the reduction of the metallic cross-section of the heating element. Tests have shown that the formation of metallic bridges within the conductor and hence electrical conductivity ceases at about a proportion of about 70% of the ceramic material, depending upon the grain size of the employed powders. In practice, it is not possible to produce any desired intermediate resistance value as the resistance value of the insulator is already substantial when the thickness of insulating material is within the molecular range.

To produce mixtures in which conducting properties and insulation properties can be controlled within a wide range, it is necessary to employ either very small quantities of insulation material due to the great insulating properties of such material or very small quantities of metal due to the high conductivity of metal.

Accordingly, it is one of the main objects of the invention to distribute insulation particles and metal particles throughout the entire cross-section of a conductor in such a manner that the resultant electrical conductivity may be of any desired intermediate value.

According to a now preferred embodiment of the invention, the powdered raw materials are pressed into shape and then sintered by subjecting the same to a heat treatment at high temperature. To attain the desired semi-conducting effect, the powders are subjected to a surface treatment before being sintered. This surface treatment consists of coating nonmetallic powders with a metallic coat.

Extensive tests seem to indicate that the observed semi-conducting properties are caused by reason of the fact that as a result of the heat treatment diffusions of the metal atoms create conducting strings or bridges of capillary size throughout the insulation material which strings or bridges reduce the insulating property of the insulation material. Semi-conductors of the type above discussed are sometimes hereinafter referred to as "capillary conductors."

The surface treatment of powder particles as employed by the invention is similar to the conventional coating of metal surfaces with protective coats so that it need not be described here in detail. The surface coating can be formed by annealing the material in gases or by a heat treatment in aqueous solutions, frequently simultaneously with an application of electric current (anodic treatment) or by an electrolytic treatment. It is also possible to produce the coats by mechanical treatment. In any event, the objects of the surface treatment is to coat metal particles with coats having a lower electrical conductivity, such as coats composed of oxides, nitrides, aluminas (aluminum oxides), carbides, and other suitable metal oxides.

It is also possible to anneal the powder in a carbonacous

atmosphere, thereby producing a coat of carbide. The previously described methods of surface treatment are not suitable for all metals, for instance tungsten is one of these not suitable metals. Such metals can be made useable in semi-conductors according to the invention by first covering the same with another metal which can be surface treated and then coating the intermediate metal coat with a coat in which the previously explained capillary conducting properties are present.

The previously described surface treatment of metals has other advantages in addition to changing the electrical conductivity. For instance, the melting point of the material will be higher so that the resistance to temperature of the semi-conductor after the sintering is no longer controlled by the metallic component only but also by the carrier or skeleton. As a result, the semi-conductors can be heated far beyond the melting temperature of the metal and until the non-metallic components begin to soften.

Another advantage of the surface treatment resides in the possibility of finishing the manufacturing process by the sintering process so that the energy then released aids the sintering process.

The previously described means of producing capillary semi-conductors offers many possibilities to obtain any desired resistance value intermediate the resistance values of metallic material by varying the factors controlling the manufacturing process. It will be evident that, among others, the following conditions can be changed; the grain size of the powder, the thickness of the coats, the applied pressure, the sintering temperature, the sintering time, and the sintering atmosphere.

The following examples will serve to explain the invention further:

(1) The surfaces of zirconium powder are oxidized by heat treatment in air at a predetermined temperature. The powder, thus prepared, is compressed with or without the application of binding means and then sintered. Tests show that the resistance of the coating against the influence of high temperatures is substantially improved, that conductors made of such material represent semi-conductors, and that after the sintering they remain solid far beyond the melting point of zirconium and also resist oxidation.

(2) Iron powder is surface treated by the conventional method of phosphorating and subsequently sintered. Tests show that the resistance against oxidation is substantially improved, and that the iron content shows capillary conducting properties.

(3) Tungsten powder having a high melting point is coated with zirconium by electrolytic means and then treated as described under No. 1. The resistance to temperature of the material thus formed is controlled by the coat of zirconium oxide so that the conductor will remain solid in air even at very high temperatures. Also, the coat possesses capillary conducting properties (the melting point of zirconium oxide being at about 2700° C.).

(4) Titanium oxide is heat treated in a carbonaceous atmosphere for the purpose of forming a metal-carbide coat and subsequently sintered in vacuum. Tests show that the finished product has capillary conducting properties.

(5) Surface treated zirconium or other less precious metals in powder form are mixed with clay for the purpose of further influencing the resistance of the surface treated material and subsequently compressed and sintered. This process is particularly advantageous when the mixed capillary conducting material is used to cover a carrier or skeleton made of clay or other non-metallic material of the same kind as the one with which the surface treated metal powder is mixed, and subsequently the coating and the carrier or skeleton are simultaneously sintered. The bonding between carrier and capillary conducting material can be made particularly strong by providing one or more intermediate coats or layers in which the proportion of metallic and non-metallic particles varies from

layer to layer according to a selected function, for instance the metallic particles may increase toward the outside. Such intermediate layers or coats serve to neutralize or equalize the internal tensions of the conductor caused by different coefficients of expansion.

The semi-conductor thus formed is preferably covered at the outside with a gas-tight ceramic coat while the core of the conductor consists of material having capillary conducting properties. Such gas tight outer coat serves to protect the conductor against oxidation, thereby increasing the life term of the conductor.

In the accompanying drawing, a semi-conductor manufactured according to the process of No. 5 is shown by way of illustration and not by way of limitation.

Fig. 1 is an elevational, partially sectional view of a heating element according to the invention, and

Fig. 2 shows a section along line 2—2 of Fig. 1.

The heating element according to Figs. 1 and 2 comprises a semi-conducting core 3 composed of capillary conducting material and clay. Core 3 is covered with several intermediate coats 4 and 5 (two being shown) also composed of capillary conductive material and clay, the clay component being increased from one coat to the other toward the outside. Coat 5 is coated with an outer coat 6 consisting of clay only. Coat 6, when heated, is harder than the capillary conducting material, thereby improving the strength of the heating element. The heating element can be connected by contact flanges 7 and 8 to an electric circuit.

A specific example of manufacturing capillary conducting material

One part by weight of aluminum powder having a grain size of 0.06 mm. diameter or less is mixed with six parts by weight of H_2O and then boiled for the purpose of forming a non-metallic surface coat until the water is completely evaporated. A weight increase of the oxidized powders by about 4% will serve as a measure for the formation of a surface coat. The powders are now mixed with clay powder having substantially the same grain size at a ratio of 1 to 1 and subsequently compressed in dry condition. The applied pressure should be in the order of one ton per $cm.^2$. A mixture as previously defined will have an electric resistance of about 10^5 to 16^6 ohm/$mm.^2$. The compressed material is then sintered in an electric furnace at about 850° to 900° C. The material can be placed in a small vessel in which is also placed carbon powder for the purpose of reducing the effect of the oxygen in the air.

The heating to the required temperature takes about 3 minutes for rods having a diameter of 10 mm. The reaction time after the heating period is about 40 to 80 seconds for a rod having a diameter of 10 mm. and a length of 60 mm. The rod can be cooled in about 2 to 3 minutes without detriment. The increase in temperature during the sintering is about 400° C., so that the sintering temperature is about 1250 to 1300° C.

What is claimed is:

1. An electrical semi-conductor formed of a sintered compressed mixture of particles of an electrically conductive metal selected from the group consisting of zirconium, titanium, iron, and aluminum, said particles being individually enclosed in a coat of a substantially non-conductive compound of said metal, said coat containing electrically conductive capillary bridges of said metal.

2. An electrical semi-conconductor consisting essentially of a compressed intimate mixture substantially composed of particles of an electrically conducting metal selected from the group consisting of zirconium, titanium, iron, and aluminum, said particles being coated with a compound of said metal selected from the group consisting of oxides and carbides, and of powdered clay in an amount not exceeding about 70 percent by weight of said mixture, said coat of said metal compound con-

taining capillary electrically conducting bridges of said metal.

3. An electrical semi-conductor consisting essentially of a compressed intimate mixture substantially composed of aluminum particles having a surface of alumina, and of clay powder in an amount not exceeding about 70 percent by weight of said mixture, said alumina surface comprising about 4 percent by weight of said particles and containing capillary electrically conducting aluminum bridges.

4. A method of manufacturing electrical semi-conductors comprising boiling aluminum particles in water until the particles have formed an alumina surface, the amount of said alumina being about 4 percent by weight of the particles, drying said particles, mixing said particles with about an equal amount of powdered clay, compressing the mixture under a pressure of the order of about 1 ton per sq. cm., and heating the compressed mixture to a temperature of about 850 to 900° C. for a time sufficient to cause diffusion of the aluminum into the oxide coat to form capillary electrically conducting bridges.

5. A semi-conductor as described in claim 3, wherein said aluminum particles have a grain size of 0.06 mm. diameter and less, and wherein said clay powder has approximately the same grain size as the metal particles.

6. An electrical semi-conductor consisting essentially of a core constituted by several concentrically disposed

layers each comprising a compressed intimate mixture composed of metal particles selected from the group consisting of zirconium, titanium, iron, and aluminum, said particles being coated with a compound selected from the group consisting of oxides and carbides of said metals bonded to said particles, said non-metallic coat containing capillary bridges formed by said metallic particles, and of powdered clay, said core being the proportion of clay relative to the coated metal particles increasing from the innermost layer toward the outermost layer and not exceeding about 70 percent by weght of the entire mixture in said outermost layer; and an outer gas-tight coat of clay surrounding said core.

7. An electrical semi-conductor formed of a compressed intimate mixture of tungsten particles coated with zirconium, the surface of said zirconium being oxidized to zirconium oxide and containing capillary electrically conducting bridges of metallic zirconium.

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