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Pitha et al.

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[54] **ELECTRODE FOR POROUS CERAMIC AND METHOD OF MAKING SAME**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 277,887, Aug. 4, 1972, abandoned.

[52] **U.S. Cl.** **117/221**, 338/21, 252/520

[51] **Int. Cl.** **B44d 1/02**

[58] **Field of Search** 117/221; 338/20, 21; 252/520, 516; 317/61

[56] **References Cited**

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[57] **ABSTRACT**

A porous ceramic is provided on its surface with an electrode comprising a titanium oxide and a more readily reduceable metal oxide.

Also disclosed is a method for applying the above electrode. The method includes the step of applying to a substrate of unfired ceramic composition a fluid suspension mixture of a titanium oxide and a metal oxide more readily reduceable than the titanium oxide. The substrate is then fired at a temperature of between 1,200° and 1,300°C until the titanium oxide is reduced to form a relatively conductive oxide comprising less oxygen than the stoichiometric form of titanium oxide.

10 Claims, 3 Drawing Figures

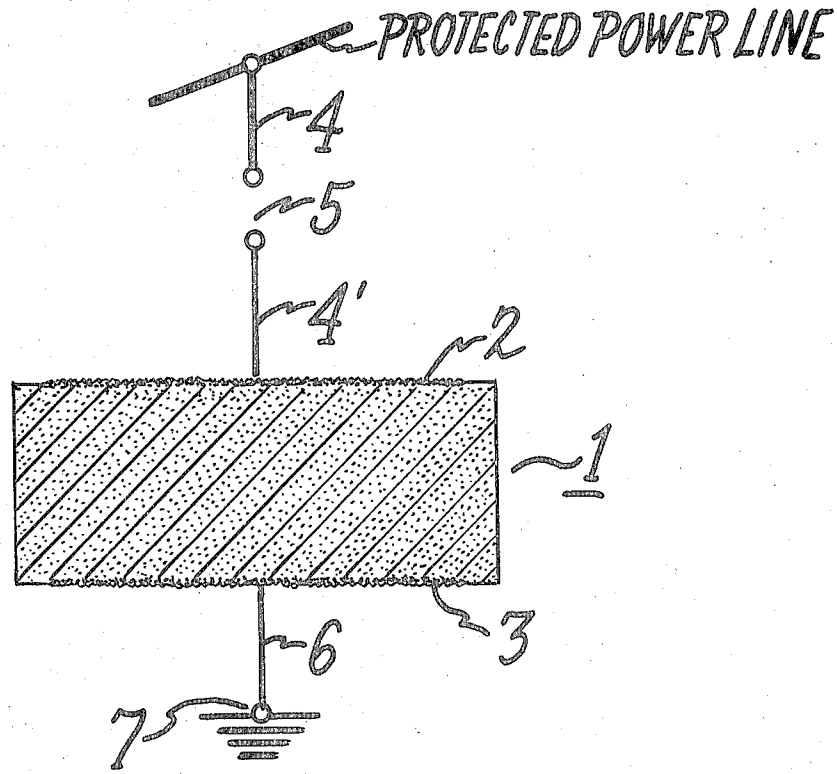


Fig. 1.

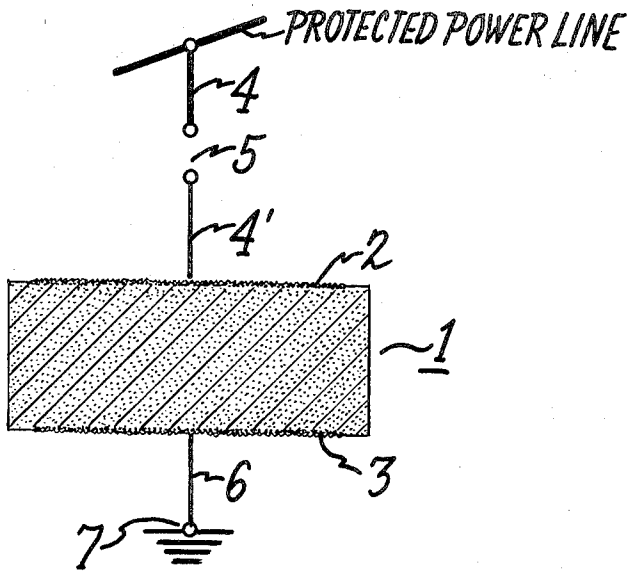


Fig. 2.

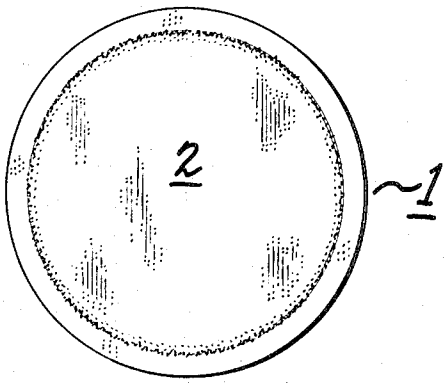
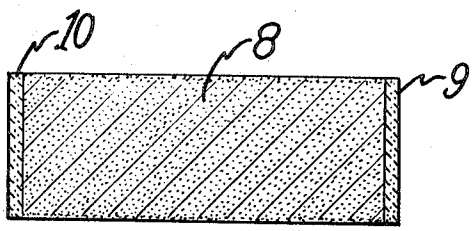


Fig. 3.



ELECTRODE FOR POROUS CERAMIC AND METHOD OF MAKING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of application Ser. No. 277,887, filed 4 Aug. 1972 and entitled "ELECTRODE FOR A GRANULAR ELECTRICAL CIRCUIT ELEMENT AND METHOD OF MAKING SAME" and now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a method for forming a low resistance electrode on a porous ceramic, such a block of non-linear resistance material, or on a molded block of granular electrical resistance material. The invention also encompasses an electrode formed on a similarly granular electrical circuit element. More particularly, the invention is well suited for forming a wear-resistant, metal-ceramic pair of electrodes on opposite surfaces of a block of non-linear resistance valve material. Such a material is silicon carbide, of a type commonly used to afford a current limiting function in high voltage surge arresters.

In the manufacture of voltage surge arresters, or so-called lightning arresters, it has become conventional to electrically connect one or more stand-off sparkgaps in series with one or more blocks of non-linear resistance valve material to form a discharge path through the arrester to a ground terminal. Various types of semi-conductor materials have been found suitable for this purpose. For example, nickel oxide, lead oxide, copper oxide and silicon carbide, as well as various ferrites and such metals as silicon and germanium are well known as effective voltage responsive resistors or semiconductors. Due to its high current-carrying capacity and relative low cost, silicon carbide is now commonly used as a non-linear resistance valve material for surge voltage surge arresters. This application of silicon carbide was disclosed, for example in U.S. Pat. No. 1,822,742, which issued to McEachron on Sept. 8, 1931. In the manufacture of valve blocks for arrester applications, the valves are usually formed of silicon carbide grains and a bonding agent molded together into disc form and then fired to form a ceramic bond between the particles of silicon carbide. Disc-shaped valves of this type must be provided with some type of electrode surface on opposite ends thereof if the flow of discharge current through the valve is to be properly distributed and thus optimized.

The electrodes formed on such disc valves should have several basic properties. Preferably, the electrodes will form a low resistance connection with the valve. Also, the electrode should be mechanically rugged so that it is not damaged by abrasion during use. Furthermore, the electrodes should be uniformly conductive so that current is evenly distributed across the entire interface between the electrodes and the granular valve disc surface.

To satisfy these requirements in recent years, it has become a relatively common practice to form electrodes on opposite surfaces of silicon carbide valve discs by spraying molten metal such as silver, copper, brass or aluminum onto a predetermined surface area of the discs. One example of such an electrode forming technique is disclosed in U.S. Pat. No. 2,501,322, which issued in Mar., 1950. But even before such molten metal spraying techniques became common in the manufacture of surge voltage surge arrester valves, it was known that relatively low-resistance terminals could be fored on a block of silicon carbide by condensing a silicon vapor on the valve to form terminals on its opposite ends. Examples of this method are shown in U.S. Pat. No. 1,842,088 which issued in January, 1932. Another U.S. Pat. No., 2,150,167 issued in March, 1939, discloses a voltage surge arrester having the porous surfaces of all the granules of a mass silicon carbide grain mounted in the arrester housing covered with a silica layer to control the flow of electric current through the arrester discharge path. Finally, in U.S. Pat. No. 2,273,704 which issued in February, 1942, there is disclosed a silicon carbide valve disc having a pair of metal plate terminals mounted on opposite sides thereof, with a non-ohmic conductor of boron carbide or silicon carbide disposed on the granules of the silicon carbide disc between it and the plate electrodes.

The foregoing examples of prior attempts to form low resistance electrodes on silicon carbide valve discs provide an indication of the strong commercial demand for such an electrode arrangement. In addition to these early attempts to provide an adequate solution to this fundamental problem, further experiments have been performed with silicon carbide compositions in somewhat related fields of art. For example, U.S. Pat. No. 2,996,415, which issued in August, 1961, discloses a method of purifying silicon carbides for a diode device by melting part of the silicon carbide with a chromite wafer in an inert atmosphere, so that the chromium wafer forms a molten chromium zone that dissolves the silicon carbide on one side of it (a hotter side) and regrows silicon carbide granules on a cooler side of it.

Beyond the field of granular non-linear valve discs, it is well known to form electrical contacts or similar conductors of pressed grains of silicon carbide or other suitable oxides. For example, in U.S. Pat. No. 868,502, issued to Stienmetz, there is disclosed an electrode for an arc lamp that is formed of powdered magnetite and granules of titanium oxide or other suitable refractory materials. As suggested in a later U.s. Pat. No., 905,557, it is known to combine granules of silicon carbide with such a pressed electrode in order to avoid flicker in the light developed by an arc that is supplied with current through the electrode. Although the techniques used in the manufacture of arc electrodes or brush type contacts is not generally regarded as directly analogous to the manufacture of molded non-linear valve discs, it is known in the manufacture of such brush-type conductors to combine carbon and metal oxides in powdered form and then reduce the oxide to form a metalgraphite contact, as disclosed in U.S. Pat. No. 1,071,044 for example. Another technique used in this conductor art involves the formation of a cold-molded batch of metal powders and a deoxidizing agent with a layer of powdered metal contact material, which is then heated to form an alloy at the interface of the contact material and the pressed metal conductor element. Such a method is disclosed in U.S. Pat. No. 2,278,592.

In addition to the problem posed by the need for making low resistance electrodes on arrester valve discs, a second problem encountered in the use of silicon carbide valve discs to form part of the discharge path in a surge arrester is due to the severe electromechanical stresses encountered in that environment.

Such stresses are caused by the inrush of thousands of amperes that must be discharged through the disc when the standoff sparkgaps of the arrester are arced over in response to a surge voltage occurring on a protected line to which the arrester is connected. These currents prodcue thermal stresses of considerable magnitude within the valve discs. Thus, it is important to provide some means for increasing the long duration strength of the discs under such thermally cycled conditions. Prior to the present invention, it was well known that various compositions of clay and metal oxides might be used to form an insulating casing around the outer surface of valve discs in an arrester housing. An example of such an insulating casing on a valve disc is shown in U.S. Pat. No. 3,207,624 which issued in Sept., 1965. As taught in that patent, such insulating casings are intended primarily to prevent flashover of the valve discs when a surge voltage is applied across the valve. However, it is possible that some mechanical strengthening of the disc might also result from the use of the baked-on clay composition casing. It is desirable, though, to provide additional specific means for assuring an improvement in long duration strength of silicon carbide discs, in order to prevent them from being cracked or otherwise ruptured by surge voltage arrester applications.

SUMMARY OF THE INVENTION

In accordance with the invention, a porous ceramic surface is provided with an electrode comprising a titanium oxide.

The novel electrode may be applied by a novel method comprising the steps of applying to the surface of a porous, granular substrate a layer of a titanium oxide. The substrate is then fired in a reducing atmosphere at a temperature of at least 1,200° C (Celsius) until the titanium oxide is reduced sufficiently to form a relatively conductive oxide having an oxygen content less than the oxygen content of the stoichiometric form of titanium oxide.

The novel electrode may be applied to an unfired, molded body of ceramic composition and is particularly useful for silicon carbide non-linear resistor elements used for over voltage protection of components, such as in surge arresters. A silicon carbide non-linear resistor provided with the novel electrode has substantially enhanced ability to discharge large blocks of power and thus has improved long durations of strength.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a side elevation view, in cross section, of a molded block of granular, nonj-linear resistance valve material that is provided with electrodes on the top and bottom surfaces thereof pursuant to the present invention. These electrodes are depicted with respect to a schematically illustrated sparkgap and electrical ground connection to illustrate an environment for the valve and its associated electrodes, similar to that presented by a voltage surge arrester application.

FIG. **2** is a top plan view of the valve disc illustrated in FIG. **1**, showing one of its electrodes.

FIG. **3** is a side view of an elongated resistor having a pair of electrodes formed on opposite ends thereof, pursuant to a second embodiment of the invention disclosed herein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that the present invention is particularly well suited to form electrodes on a porous ceramic molded block of non-linear resistance valve material similar to the disc-shaped block **1** illustrated in FIG. **1** of the drawing. In the preferred embodiment of the invention, the valve comprises a body **1** that is generally cylindrical in form. Pursuant to the invention, a pair of electrodes **2** and **3** are affixed to the valve body **1** on opposite sides of it; in the case illustrated, on the top and bottom surfaces. It should be appreciated that any suitable granular electrical circuit device might be substituted for the valve disc **1**, in practicing the invention in alternative embodiments. For example, an electrical resistor or other structure might be used as a base surface for electrodes **2** and **3**, in lieu of the valve **1**.

In this form of the invention, the non-linear resistance valve **1** is formed of grains of silicon carbide which may be of any suitable commercially available form similar to that commonly utilized in the manufacture of valve elements for voltage surge arresters. As explained hereinafter, the valve disc **1** is formed by molding a porous, granular body of unfired ceramic composition, a composition which when fired will form a ceramic structure, in a molding and then firing the body in order to bind the granules of silicon carbide together with a ceramic or glass-interface bond, as is well known in the art. It is important to note that the electrodes **2** and **3** are applied to predetermined surface areas of the top and bottom of valve disc **1**, so that current applied to these electrodes is distributed across substantially the entire circular surfaces of the disc **1**. This arrangement of the top electrode **2** in relation to the upper edge of the valve disc **1** is best seen in FIG. **2**. As shown, the electrode **2** terminates short of the edge of disc **1**, in order to reduce the risk of a flashover of the disc **1** when a voltage surge is applied between electrodes **2** and **3**. Of course, the areas selected for applying the electrodes **2** and **3** on valve disc **1** are disposed in spaced-apart relationship on substantially opposite surfaces of the valve **1**. Accordingly, when disc **1** is connected in a voltage surge arrester application, such as that shown schematically by the circuit of FIG. **1**; including a connecting line **4–4'** and a standoff sparkgap **5**, as well as a second connecting line **6** and ground terminal **7**, it forms a discharge circuit that passes current through the entire body of the valve **1**.

The invention is described herein with particular reference to such a voltage surge arrester application because the electrodes **2** and **3** that are provided by it for the valve disc **1** are particularly advantageous in that they form a strengthening bond with the granular surfaces of the disc **1** thereby to substantially enhance the long duration strength of the valve **1** to electromechanical stresses resulting from the discharge of large overcurrents through such a valve. It has been found that the electrode **2** and **3** formed by the present invention comprise a so-called cermet, or ceramic-metal, layer on opposite surfaces of the valve disc **1**, in intimate contact with the granules of these surfaces.

It should be understood that although silicon carbide is used in the preferred embodiment of the invention to form the valve **1**, the body of valve **1** could be constituted of any suitable mass of carbide grains taken from the class consisting of silicon carbide, tungsten carbide

and boron carbide. Then, pursuant to the invention, this body is placed in combination with at least one electrode (such as electrode 2 or 3) that comprises a composition consisting of 31 percent by weight of Ti, 20 percent of Cr as free metal or as intermetallic amorphous compounds in a matrix.

Now, in order to further explain the novel features of the invention, some examples will be given of a preferred method for practicing the invention. In general, suitable electrodes can be formed by the invention by applying the novel electrode compositions to either a cured, or an unfired, block or body of granular, or porous ceramic material, such as pressed silicon carbide. In the preferred embodiment of the method of the invention, the electrode composition is applied to an unfired, molded disc of silicon carbide, which is subsequently fired in conjunction with the firing of the electrode composition as will be more fully described below.

EXAMPLE 1

In the first example of the method of my invention, it will be assumed that at least one electrode is to be applied to a pre-fired molded body of non-linear resistance valve material such as the valve disc 1 of silicon carbide illustrated in FIG. 1. In addition, to providing such a porous ceramic body, the process of the invention requires one to apply to a predetermined surface area of the body 1 an electrode composition consisting of 20 to 40 percent by weight chromic oxide (Cr_2O_3), 50 to 70 percent by weight titanium dioxide (TiO_2) and 5 to 10 percent by weight clay, which is mixed with water to a suitable fluid consistency. The fluidized electrode composition may be applied to the disc 1 by spraying, painting, or a suitable silk screening process is well known in the art. After the electrode composition is thus applied to the predetermined surface of disc 1, the disc is placed in a reducing atmosphere and the electrode composition is fired at 1,200° to 1,300° C until the TiO_2-Cr_2O_3mixture is reduced to an electrically conductive layer. Finally, the electrode composition and disc 1 are cooled to room temperature. In practicing the invention, it has been found that a reducing atmosphere of substantially pure hydrogen is suitable for the intended purpose. Of course, alternative reducing atmospheres such as an atmosphere of cracked ammonia or other hydrogen-rich atmospheres may be used. The reducing atmosphere should comprise at least 50percent to 100percent by volume of the atmosphere in which the electrode composition is fired to form electrode 2 on disc 1.

In the first example of the method of my invention, where the valve disc 1 is pre-fired, it is only necessary to continue the firing operation long enough to substantially reduce the $TiO_2$and Cr_2O_3. It has been found that such a reduction takes place when the firing temperature is maintained at at least 1,200°C for at least 1 hour.

EXAMPLE II

In a second example of the method of my invention, a pair of electrodes were formed on a porous ceramic body of molded silicon carbide which was not prefired. To predetermined surface areas of this body of uncured silicon carbide material there was applied an electrode composition consisting of 50 to 95 percent $TiO_2$by weight, and 5 to 50 percent clay by weight, mixed with water to a fluid consistency. The porous body 1 and the electrode composition were then fired at a temperature of at least 1,200°C in a reducing atmosphere until a ceramic bond was matured in the body 1. In practice, such a ceramic bond is uniformly formed in such discs after they are fired at the foregoing temperature for at least one hour. Finally, the disc 1 and the resultant electrodes 2 and 3 were cooled to room temperature.

As a result of the experimentation with the various electrode compositions described above, an optimum electrode composition was found to consist essentially of 35 percent by weight Cr_2O_3, 60 percent by weight $TiO_2$and 5 percent by weight clay, which is mixed with water to a fluid consistency, applied and fired in the manner described above with reference to the first example.

GENERAL CONSIDERATIONS

The electrode as described herein is suitable for applying to porous ceramics other than silicon carbide as described in the preferred embodiment. The term "porous granular substrate" as used herein refers to both porous ceramics and to porous unfired ceramic compositions. It may be applied also, for example, to tungsten carbide or boron carbide. It is, however, particularly useful for silicon carbide blocks use for non-linear resistor applications, since the reducing of the oxide takes place at much the same temperature as the sintering process for forming the silicon carbide ceramic itself from the unfired silicon carbide, which is in the form of a moleded porous granular body. Thus, no additional heat processing is required for applying such electrodes on silicon carbide blocks, since the electrode is formed during firing of the ceramic composition.

A titanium oxide is used in the oxide mixture because such an oxide will reduce properly at the required temperatures for heat treating the silicon carbide ceramic during its manufacture. While the exact nature of the phenomena occurring during the forming of the electrode is not completely understood, it is thought that as the oxide of titanium becomes progressively more reduced by the removal of oxygen atoms, the structure of the oxide passes a state of stoichiometric composition to a state having a large number of crystal lattice defects, which result in the increased conductivety desired for electrode applications. While a reduced titanium oxide alone can function as an electrode, it is desirable to mix with it a more easily reduced metal oxide. The metal and its oxide should have a relatively high vapor pressure at the desired firing temperature of 1,200° –1,300°C and be relatively corrosion resistant in the environment to which the finished electrode is to be subjected. Examples of metal oxides more readily reduceable than titanium oxide, and which are considered particularly suitable for this purpose, are oxides of chromium, iron, copper, and nickel, either alone or mixed. The addition of the readily reduced metal oxide to the mixture for forming the electrode provides an electrode which is more rugged and more conductive than one from titanium. where the electrodes are used on silicon carbide elements for surge arrester applications, as in the preferred embodiment, an oxide of chromium appears to be particularly suitable for use together with the titanium oxide.

While a certain amount of more readily reduceable metal oxide improves the electrode when added to the

titanium oxide, the amount added should be limited. Too great a percentage of the added oxide will result in undesirable mechanical surface stressing due to shrinking, leading to cratering of the electrode layer.

In the preferred embodiment, the metal oxide mixture was applied to the surface of the ceramic by forming a suspension in water with clay. The clay has a function of acting as a suspending agent. It should be understood that other suspending agents may be used for this purpose. For example, magnesium silicate is a known suspending agent. a number of suspending agents are commercially available known alternatives to clay. Clay, however, has particularly advantageous characteristics for the electrode of the preferred embodiments in that it appears to aid in forming the desired structural characteristics of the electrode composition and may also improve the electrical characteristics. The particular type of clay used to gain these added benefits is not considered critical, but the clay should be an electrical grade clay.

The term "oxide" as used herein refers to any of the various oxide forms of the particular metal in question. For example, titanium oxide may be titanium monoxide or dioxide, as well as sub-oxide forms. The oxide as applied should be finely divided, that is having particles no larger than 200 mesh size.

We claim:

1. A method of forming an electrode on a porous ceramic substrate comprising the steps of:

applying to the surface of a porous, granular substrate a layer of a finely divided titanium oxide;

heating the substrate with the applied layer in a reducing atmosphere to a temperature of between 1,200° to 1,300°C until the titanium oxide is reduced more than it is in its stoichiometric state and becomes relatively conductive, and

cooling the substrate to room temperature.

2. The method defined in claim **1** and wherein there is mixed with the titanium oxide an added metal oxide which is more readily reduceable than is the titanium oxide.

3. The method defined in claim **2** wherein the substrate is an unfired ceramic composition.

4. The method defined in claim **3** wherein the added oxide is an oxide of chromium.

5. The method defined in claim **4** wherein said substrate is a pressed body of silicon carbide particles held by a binder.

6. The method defined in claim **5** wherein the titanium oxide is present in the oxide mixture to between 50 and 90 percent by molecular weight and the added metal oxide is present to between 0 and 40 percent by molecular weight.

7. The method defined in claim **6** wherein the titanium oxide and the added oxide are suspended in a fluid with a suspending agent prior to said applying.

8. The method defined in claim **7** wherein the fluid is water and the suspending agent is clay present to between 5 and 10 percent by molecular weight in the mixture.

9. A method as defined in claim **8** wherein said reducing atmosphere is formed of gas from the class of hydrogen and cracked ammonia, and comprises at least 50 to 100 percent by volume of such gas.

10. A method as defined in claim **9** wherein the firing operation is continued for at least 1 hour at at least 1,200°C.

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