

[54] **ELECTRODE FOR A GRANULAR ELECTRICAL CIRCUIT ELEMENT AND METHOD OF MAKING SAME**

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Related U.S. Application Data

[62] Division of Ser. No. 277,887, Aug. 4, 1972, abandoned.

[52] U.S. Cl. **338/21, 29/621, 252/516, 338/327**

[51] Int. Cl. **H01c 7/12**

[58] Field of Search **338/21, 20, 327, 330; 117/224, 227; 29/621; 252/516; 317/234 L**

References Cited

UNITED STATES PATENTS

2,914,742 11/1959 Hoath 338/21

3,096,496 7/1963 Burrage et al. 338/21
3,360,761 12/1967 Stapleton et al. 338/330
3,716,407 2/1973 Kahn 117/224

Primary Examiner—C. L. Albritton

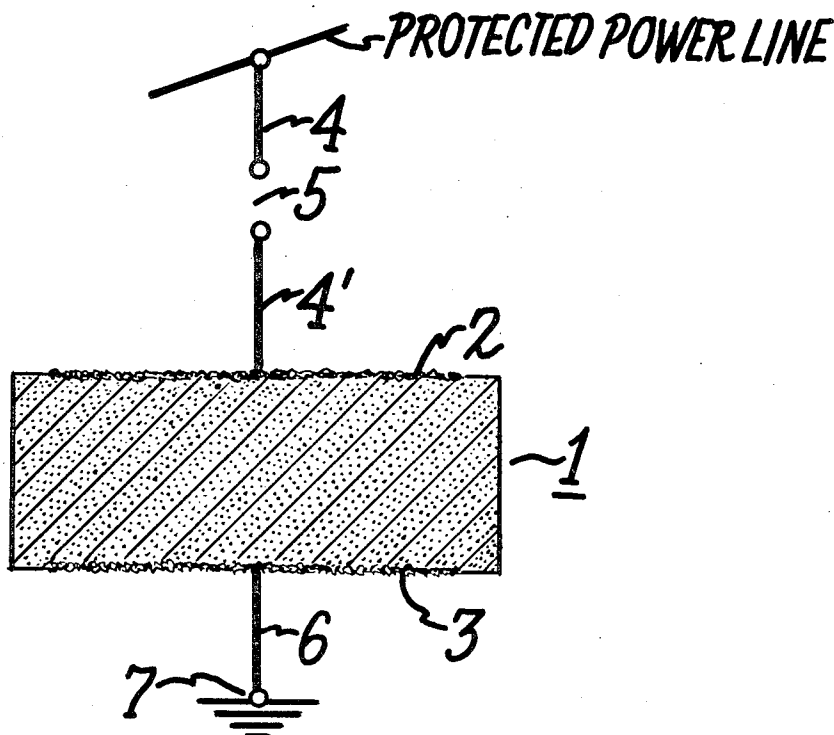
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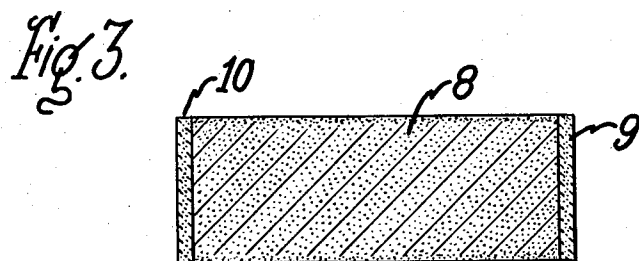
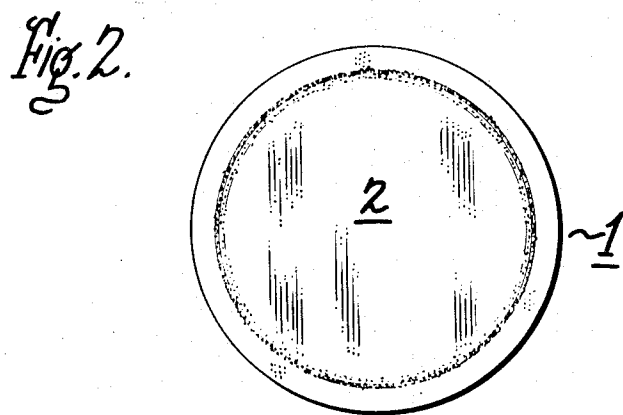
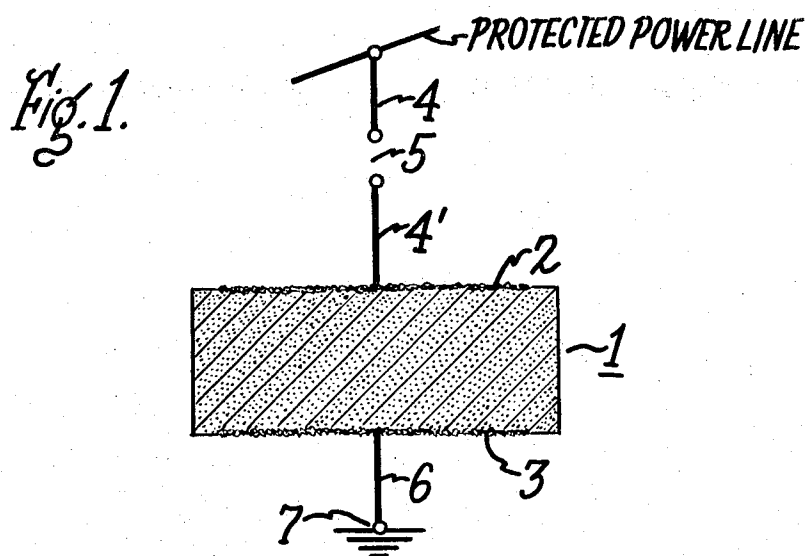
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ABSTRACT

A ceramic-metal electrode is provided on the granular surface of a block of non-linear resistance material such as silicon carbide. The electrode forms a low resistance electrical contact with granules of the silicon carbide, and is manufactured by applying a water-moistened composition of an easily reducible, refractory metal oxide, in combination with a suitable clay, to predetermined areas of the non-linear material. The electrode composition is then fired in a reducing atmosphere to form a ceramic-metal electrode that affords excellent electrical conductive properties and provides a bond to the surface of the material, thereby to improve its long duration strength.

4 Claims, 3 Drawing Figures





ELECTRODE FOR A GRANULAR ELECTRICAL CIRCUIT ELEMENT AND METHOD OF MAKING SAME

This is a division of application Ser. No. 277,887, filed Aug. 4, 1972 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a method for forming a low resistance electrode on 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 surge voltage 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 semi-conductors. 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 arresters. This application of silicon carbide was first taught by McEachron in U.S. Pat. No. 1,822,742, which issued on Sept. 8, 1931. In the manufacture of valve blocks for arrester applications, the valves are usually formed of a silicon carbide grain and a bond system that is molded into disc form and then fired to form a ceramic bond between the particles of silicon carbide, as taught by McEachron. 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 arrester valves, it was known that relatively low-resistance terminals could be formed 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 Jan., 1932. Another U.S. Pat. No. 2,150,167, that issued in Mar., 1939, discloses a lightning arrester having the porous surfaces of all the granules of a mass of 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 Feb., 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 a good 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 Aug., 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 Steinmetz, 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 metal-graphite 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 lightning arrester is due to the severe electro-mechanical 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 produce 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. Accordingly, it is a primary object of the present invention to provide a method for forming an improved electrode that is ideally adapted for use with a porous electrical circuit element, such as a resistor or a semiconductor device. In addition, the invention teaches the construction of such a novel electrode in combination with a granular body member.

SUMMARY OF THE INVENTION

In a preferred form of the invention, an electrode is formed on a molded body of granular semiconductor material by providing a composition of easily-reduced oxides of a refractory metal mixed with a suitable clay, then the composition is moistened to a fluid consistency before applying it with a spraying, brushing or other conventional technique to predetermined surface areas of the granular body. Next, the composition is fired in a reducing atmosphere until the metal oxide is reduced to an electrically conductive state. In practicing the method of the invention, the electrode composition may be applied to either a cured, molded body, or to an unfired molded body. The electrode formed by this process affords a surface bonding condition for the valve disc that substantially enhances its ability to discharge large blocks of power, that is, the long duration strength of the valve disc. Thus, the resultant electrode and combined electrical circuit element form a part of the present invention.

One object of the present invention is to provide an improved electrode for a granular electric circuit element, that affords an optimum solution to the problems of related prior-art electrodes that are discussed above.

Another object of the invention is to provide an improved non-linear resistance valve element and associated electrodes for a surge voltage arrester application.

Still another object of the invention is to provide an improved method for forming electrodes on a molded, granular electric circuit element.

Yet another object of the invention is to provide an improved electrode composition for use with non-linear resistance valve elements for surge voltage arrester applications.

A further object of the invention is to provide an electrode for a molded, granular valve disc that is effective to appreciably increase the long duration strength

of such a disc when it is subjected to the stresses resulting from the discharge of large currents through it.

Additional objects and advantages of the invention will become apparent to those skilled in the art from the description of it that follows taken in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side elevation view, in cross section, of a molded block of granular, non-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 surge voltage 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 molded block of non-linear resistance valve material similar to the discshaped 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, such as a contact member, 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 surge voltage arresters. As explained hereinafter, the valve disc 1 is formed in a molding and firing operation 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 surge voltage 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 surge voltage 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 surge voltage 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 electro-mechanical stresses resulting from the discharge of large overcurrents through such a valve. It has been found that the electrodes 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. This unique cermet bond comprises a high proportion of chromium or other substantially pure metal conducting suboxides, and intermetallic compounds, that is the result of reducing the metal-oxide electrode composition of the invention, in the manner that will be described in detail below. Thus, a pair of durable and low resistance electrodes 2 and 3 are formed by the cermet layers resulting from the forming process of the invention.

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 as intermetallic amorphous compounds in a matrix. Throughout the description of the invention disclosed herein, it should be understood that the clay utilized in the preferred embodiment of the invention may be either Kaolin clay, Kentucky Old Mine No. 4 clay, or any other suitably pure, electrical grade clay.

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. Also, although water is used herein as an agent for fluidizing the electrode composition, it will be apparent that other suitable fluids may be utilized to afford this function.

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 Cr_2O_3 , 50 to 70 percent

by weight 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 as 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°C to 1,300°C until the TiO_2 - Cr_2O_3 mixture 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. It is important to note that the reducing atmosphere should comprise at least 50 to 100 percent 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.

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 pre-fired. To predetermined surface areas of this body of uncured silicon carbide material 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, was applied. 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 4 hours. Finally, the disc 1 and the resultant electrodes 2 and 3 were cooled to room temperature.

In still another example of the method of my invention, a pair of electrodes were painted on opposite faces of a porous molded disc of silicon carbide by applying a water moistened electrode composition consisting of 20 to 40 percent by weight Cr_2O_3 , 50 to 70 percent by weight Fe_2O_3 and 5 to 10 percent by weight clay, to the preselected surfaces of the disc 1. These electrode compositions were then fired at 1,200°C to 1,265°C in a reducing atmosphere until the Cr_2O_3 and Fe_2O_3 were reduced to the electrically conductive cermet. The resultant electrodes (2 and 3) and valve disc (1) were then cooled to room temperature.

In a fourth example of the method of my invention, carbon was substituted for the Fe_2O_3 in the electrode composition of the third example described above and the operating steps of that example were performed in a similar manner with excellent results. In various other sample batches that were formulated to establish an optimum form of the invention, various easily reducible metal oxides of refractory metals were substituted for the TiO_2 used in the first example of the method of the invention described above, and the procedural steps of that example were repeated to successfully form a de-

sirable cermet electrode on a porous, granular electrical circuit device, such as the valve disc 1.

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.

Although the foregoing examples of the method of my invention are quite specific, it should be understood that the method of the invention provides an optimum means of increasing the long duration strength of a block of porous, granulated semi-conductor material, which method, in general, comprises forming a mixture of at least one compound selected from the group consisting of readily reducible oxides of a refractory metal and a mixture of clay, then tempering the mixture with a liquid, such as water, and mixing it to a fluid consistency. Next, the electrode composition mixture is disposed on one or more predetermined surfaces of the semiconductor block and heated to a temperature above $1,200^\circ\text{C}$ in a reducing atmosphere. This heating step is required to reduce the electrode compound to form a ceramic-metal electrode that is intimately bonded to the granular surface of the block. Thus, both a novel method and unique electrode structure has been disclosed, which may be adapted to many different types of electrical circuit elements, such as resistors, contactors, etc.

While the particular examples of the invention described herein proved to be highly successful in attaining the expressed purposes of the invention, variations of the disclosed ingredients within the limits specified is possible.

Therefore, while I have described a particular embodiment of the invention, it will be obvious to those skilled in the art that various changes and modifications

can be made therefrom without significantly departing from the true scope and spirit of the invention. For example, as shown in FIG. 3 of the drawing, an electrical resistor element 8 comprising a molded body of porous, granular material may be formed with a spaced-apart pair of electrodes 9 and 10 on opposite ends thereof, by the method of the invention. The only significant difference in practicing the invention with the resistor 8, as compared with the semi-conductor 1 illustrated in FIG. 1, is that the electrical properties of the resistance elements 8 may differ from the electrical properties of the semi-conductor 1. Otherwise, the mechanically strong and the electrically low-resistance cermet electrodes 9 and 10 are similar to the electrodes 2 and 3 depicted in the embodiment of the invention shown in FIG. 1.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A non-linear resistor having a body constituted of a mass of carbide grains of the class consisting of silicon carbide, tungsten carbide and boron carbide, in combination with at least one low resistance electrode affixed to a predetermined surface area of said body in electrical conducting relationship therewith, said electrode comprising a composition consisting of at least 30 percent by weight of Ti and 20 percent by weight of Cr contained in a matrix.

2. An invention as defined in claim 1 including a second electrode affixed to a second predetermined surface area of said body in electrical conducting relationship therewith, said first and second areas being disposed in spaced-apart relationship.

3. An invention as defined in claim 2 wherein said electrodes are affixed to said body on opposite sides thereof, respectively.

4. An invention as defined in claim 3 wherein said body is generally cylindrical in form, and said electrodes are affixed, respectively, to the ends thereof.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,864,658
DATED : February 4, 1975
INVENTOR(S) : John J. Pitha and Howard F. Ellis

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

At column 1, line 39, delete "a".
At column 2, line 19, change "a" to --an--.
At column 5, line 36, after "metal", insert --or--.

Signed and Sealed this
sixteenth Day of September 1975

[SEAL]

Attest:

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