

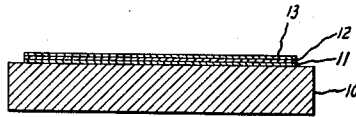
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BLOCKING LAYER FOR TITANIUM OXIDE RECTIFIER

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BLOCKING LAYER FOR TITANIUM OXIDE RECTIFIER

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This invention relates to a titanium dioxide alternating current rectifier; more particularly, it refers to a titanium dioxide rectifier having a blocking layer applied by electrolytic anodization.

In the copending application of Le Loup and Marinace, Serial No. 289,247, filed May 22, 1952, which is assigned to the same assignee as the present invention, a titanium dioxide rectifier is described together with a method for producing such a rectifier. In accordance with this copending application, a titanium rectifier is produced by heat treating a titanium plate in an atmosphere containing oxygen to produce an oxide layer, further treating the titanium plate to partially reduce the oxide layer, and applying over the partially reduced oxide layer a counterelectrode composed of a metal having a high work function.

It is an object of this invention to provide a titanium dioxide rectifier having a titanium dioxide blocking layer which confers improved rectification characteristics upon the rectifier.

It is another object of this invention to provide a method whereby a uniform blocking layer may be incorporated in a titanium dioxide rectifier.

Briefly stated, in accordance with one embodiment of this invention, a titanium plate is subjected to a heat treatment in an oxidizing, or partially oxidizing, atmosphere to produce an oxide layer over at least a portion of the titanium plate surface. The partially oxidized layer is then subjected to an electrolytic anodization treatment to provide a thin uniform blocking layer of oxide to which an overlying layer of counterelectrode metal having a high work function is then applied.

The drawing is a sectional view illustrating one embodiment of my invention. A base electrode 10 is composed of a titanium plate thick enough to impart rigidity to the device. Overlying all or a part of the titanium plate 10 is a partially oxidized layer 11. The exposed surface of the layer 11 is subjected to an electrolytic anodization treatment which results in the formation of a thin layer 12 of oxide. Overlying all or a portion of the layer 12 is a counterelectrode layer 13 composed of a metal having a high work function.

The thickness of the layers 11, 12 and 13 is greatly exaggerated for purposes of clarity of illustration. The layers 11 and 12 are normally less than a thousandth of an inch in thickness and the layer 13 may be of the order of a thousandth of an inch. The base electrode 10 may be much thinner than it is shown in the illustration.

In preparing a titanium dioxide rectifier in accordance with my invention, the titanium plate 10 must have a clean surface. This may be obtained by subjecting a plate to an abrasive process or by treatment in an acid solution. A satisfactory acid solution in which the plate may be immersed consists of 80% nitric acid and 20% hydrofluoric acid.

The plate is then subjected to a heat treatment in an atmosphere containing oxygen. The high melting

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point of titanium enables this treatment to be carried out at an extremely high temperature. However, above 800° C. the rate of oxidation becomes a little difficult to control due to the fact that it takes place rather rapidly. Below 600° C. the rate of oxidation is quite slow necessitating prolonged treatment. I prefer to carry out the oxidation between 600° C. and 800° C., within which range the time of treatment varies from about two to five hours. However, it must be emphasized that there is nothing critical about the temperature and time of treatment. If the treatment temperature is above 800° C., for example 1200° C., the time of treatment may be of the order of a few minutes. If the treatment temperature is below 600° C., for example 300° C., the time of treatment is many hours or even days.

Air and steam are both satisfactory oxidizing atmospheres but of the two steam is preferable. It is necessary that the layer 11 contain some reduced titanium dispersed therethrough. Consequently if the layer 11 is provided by an air oxidation treatment, there must also be a heat treatment in a reducing atmosphere, such as hydrogen, to provide the free titanium necessary for rectification action. This may be provided by a heat treatment at the same temperature as the oxidation treatment in an atmosphere of hydrogen.

If the oxygen containing atmosphere is provided by steam, reducing action is provided by the hydrogen produced in the decomposition of the water vapor molecule. For each atom of oxidizing oxygen, two atoms of reducing hydrogen are produced. Thus the steam treatment produces a layer 11 having minute particles of titanium dispersed therethrough. The layer 11 should preferably have a thickness of the order of 0.0005".

While the base electrode 10 is shown with the layer 11 covering a portion of one surface thereof, in practice the layer 11 covers the entire surface of the titanium base 10 since it is most easily manufactured with this construction.

After the reduction step the layer 11 is subjected to an electrolytic anodization in order to provide a blocking layer of oxide. It is well known that an oxide layer applied by electrolytic anodization is self-insulating. Thus, after the oxide layer on a particular portion of the layer 11 has been built up to a particular thickness, no more current will flow through this portion and further oxidation, if any, will take place only on portions of the surface having a thinner oxide layer. This action results in an oxide layer of uniform thickness over the entire surface.

Anodizing solutions are well known in the electrolytic art. Solutions of sodium hydroxide, potassium hydroxide, chromic acid, ammonium hydroxide, and sulfuric acid are all satisfactory for purposes of applying an oxide blocking layer to the partially oxidized layer 11. I have obtained best results from the use of a sodium hydroxide solution of about 10 to 17 percent concentration. The base electrode 10 is made the anode in such a solution. The current density is a function of time (at constant voltage) and the back voltage of the cell is dependent on the final current density. The anodization is preferably accomplished by gradually increasing the potential to about 40 volts while keeping the current at about 5 ma./cm.². Under continued application of 40 volts, the current decreases to a range of 5-20 ma. on a plate 1" x 3/4". The anodization may be carried out with the solution at room temperature.

After the anodization step has been completed, the counterelectrode 13 is applied by any method which will insure the close union of the layers 12 and 13. The method of effecting a close union between the layers 12

and 13 is dependent to some extent upon the nature of the counterelectrode metal used. Certain metals may be applied in a molten state while others are best applied by vapor deposition. In general, vapor deposition is a preferred method of applying the layer 13.

It has been previously mentioned that the counterelectrode 13 is composed of a metal having a high work function. Bismuth, nickel, and platinum fulfill these requirements whereas cadmium, zinc, tin, aluminum, and magnesium when used as counterelectrodes, produce a rectifier which is considerably inferior to a rectifier having a counterelectrode composed of bismuth, nickel, or platinum. A possible explanation for this behavior lies in the fact that the partially oxidized titanium is an "n" type semi-conductor with the free titanium contributing the electron conduction. The counterelectrodes of bismuth, nickel, or platinum all have missing electrons in their "d" shells which contribute holes for a "p" type conduction. The other metals mentioned do not have missing electrons in their "d" shells. Accordingly, as used herein, the term "high work function" includes metals having missing electrons in their "d" shells which contribute holes for "p" type conduction.

The deposition of the counterelectrode on the "n" type titanium establishes a "p-n" junction. When the plates are anodized after a partial oxidation, there is a thin insulating layer, or a layer with fewer "n" or "p" carriers between the "n" type region and the "p" type region. This layer reduces the leakage and raises the reverse voltage of the rectifiers.

Of the satisfactory counterelectrodes previously enumerated, I prefer to use bismuth as this element has a low melting point which makes it easy to handle and a thin layer of bismuth allows the plate 10 to arc through at a weak spot without destroying the rectifying properties of the device. A rectifier made in accordance with my invention has superior high temperature stability and compares favorably with other rectifiers from the standpoint of current loading and voltage rating.

While the present invention has been described with reference to particular embodiments thereof, it will be understood that numerous modifications may be made by those skilled in the art without actually departing from the invention. Therefore, I aim in the appended claims to cover all such equivalent variations as come within the true spirit and scope of the foregoing disclosure.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of preparing a titanium dioxide rectifier which comprises forming a partially oxidized layer on a surface of a titanium plate by heating said plate in an atmosphere containing oxygen, forming a layer of oxide on said partially oxidized surface by electrolytic anodization and applying to said oxide layer a counterelectrode metal having a high work function.

2. The method of preparing a titanium dioxide rectifier which comprises forming a partially oxidized layer on a surface of a titanium plate by heating said plate

in a steam atmosphere, forming an oxidized layer on said partially oxidized layer by electrolytic anodization and applying to said oxidized layer a counterelectrode metal having a high work function.

3. The method of preparing a titanium dioxide rectifier which comprises forming a partially oxidized layer on a surface of a titanium plate by heating said plate to a temperature in excess of 600° C. in an atmosphere of steam for four hours, forming an oxidized layer on said partially oxidized layer by electrolytic anodization and applying to said oxidized layer a counterelectrode metal having a high work function.

4. The method of preparing a titanium dioxide rectifier which comprises forming a partially oxidized layer on a surface of a titanium plate by heating said plate in an atmosphere containing oxygen, forming an oxidized layer on said partially oxidized layer by electrolytic anodization in an aqueous sodium hydroxide bath and applying to said oxidized layer a counterelectrode metal having a high work function.

5. The method of claim 4 wherein the concentration of the sodium hydroxide solution is between 10% and 17% and the anodization is carried out at room temperature.

6. The method of preparing a titanium dioxide rectifier which comprises forming a partially oxidized layer on a titanium plate by heating said plate in an atmosphere containing oxygen, forming an oxidized layer on said partially oxidized layer by electrolytic anodization in a chromic acid solution and applying to said oxidized layer a counterelectrode metal having a high work function.

7. The method of preparing a titanium dioxide rectifier which comprises forming a partially oxidized layer on the surface of a titanium plate by heating said plate in an atmosphere containing oxygen, forming an oxidized layer on said partially oxidized layer by electrolytic anodization in an ammonium hydroxide solution and applying to said oxidized layer a counterelectrode metal having a high work function.

8. The method of preparing a titanium dioxide rectifier which comprises forming a partially oxidized layer on a surface of a titanium plate by heating said plate to a temperature between 600° C. and 700° C. in an atmosphere of steam for about four hours, forming an oxidized layer on said partially oxidized layer by electrolytic anodization in sodium hydroxide solution and applying to said oxidized layer a counterelectrode composed of bismuth.

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