April 28, 1953 A. M. SUGGS ET AL 2,636,856

ELECTRODE FOR ELECTROCHEMICAL OXIDATION

Filed June 29, 1948

Fig. 1

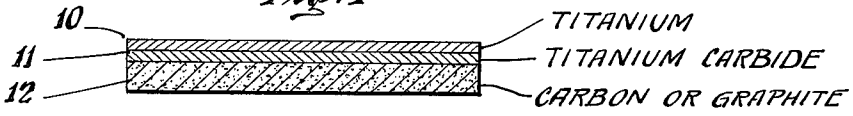


Fig. 2

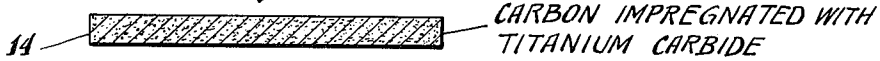


Fig. 3

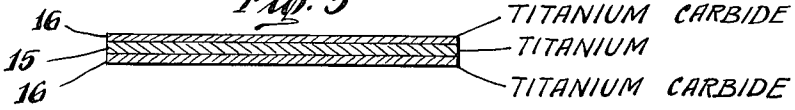


Fig. 4

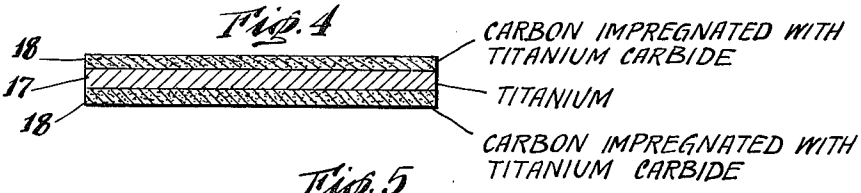


Fig. 5

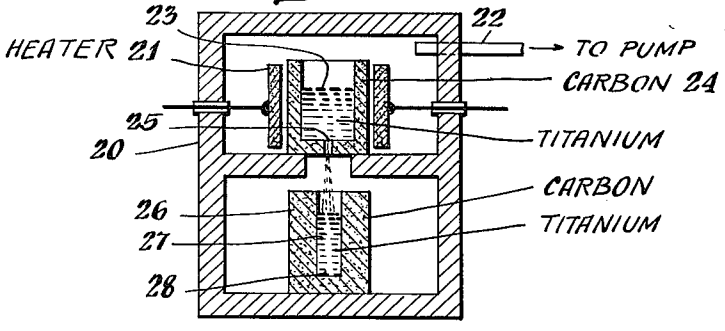


Fig. 6

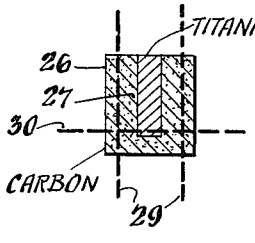


Fig. 7

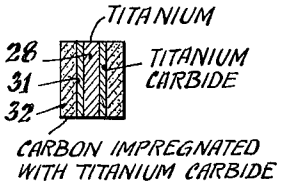


Fig. 8

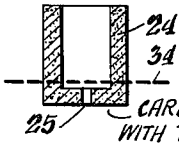
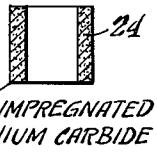


Fig. 9



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ELECTRODE FOR ELECTROCHEMICAL OXIDATION

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1 Claim. (Cl. 204—290)

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This invention relates to materials containing titanium and carbon, and, more particularly, to materials containing titanium carbide and at least one of the elementary constituents thereof.

It is an object of the present invention to provide shaped bodies including titanium carbide and at least one of the elements of carbon and titanium in a stratified or interspersed arrangement, said bodies being characterized by high resistance to heat and to various chemical influences.

It is another object of the present invention to provide electrically conducting bodies and electrodes of improved character comprising titanium carbide interspersed with or bonded to titanium, graphite, or both, for the purpose of electrolytic and primary cells, space discharge devices, such as particularly vacuum tubes, pressure applying and sliding electrical contacts, and the like.

It is a further object of the invention to provide an improved electrode for electrolytic cells, particularly useful in electrolytic cells for producing electrolytic manganese dioxide from manganese sulphate solutions containing sulphuric acid, the said electrode comprising a layer of metallic titanium coated on both faces thereof with a layer of titanium carbide.

It is also within the contemplation of the present invention to provide an electrode of novel and improved character comprising a shaped porous body of graphite which is substantially fully impregnated with titanium carbide.

The invention also contemplates various methods of making titanium and carbon compositions of the described character on a practical and industrial scale at a low cost.

Other and further objects and advantages of the invention will become apparent from the following description, taken in conjunction with the accompanying drawings, in which

Figure 1 is a longitudinal sectional view of a composite body embodying the invention and comprising titanium, titanium carbide and carbon layers;

Figure 2 is a similar view of a composition comprising a porous layer of carbon or graphite impregnated with titanium carbide;

Figure 3 is a sectional view of an electrode including a layer or core of metallic titanium coated with a layer of titanium carbide;

Figure 4 is a sectional view of an electrode comprising carbon and titanium layers the boundary surface of carbon and titanium being characterized by the presence of titanium carbide which

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also impregnated the remainder of the carbon layer;

Figure 5 is a vertical sectional view, somewhat diagrammatic and fragmentary in character, of an apparatus for carrying a preferred method of the present invention into practice;

Figure 6 is a vertical sectional view of graphite mold with a body of metallic titanium cast into a cavity thereof;

Figure 7 is a similar view of the mold shown in Figure 6 after its portions unimpregnated with titanium carbide have been removed;

Figure 8 is a vertical sectional view of a cylindrical crucible, the side and bottom walls of which are fully impregnated with titanium carbide; and

Figure 9 is a similar view of the crucible shown in Figure 8 after its bottom portion has been cut off to provide a hollow cylindrical electrode shell.

As is known, when carbon, preferably in the form of graphite, is heated with molten titanium, titanium carbide, TiC, is formed at the surface of contact. It has now been discovered that when such contact is carried out in an inert atmosphere, or in vacuum, the molten titanium wets the graphite and impregnates it to a considerable depth, completely filling the pores thereof. In this way there is formed, on cooling, a novel composition or composite body which comprises a layer of metallic titanium, a layer of titanium carbide which extends continuously into the pores of a graphite layer and firmly attaches the impregnated graphite layer to the titanium layer, and finally a layer of unimpregnated graphite.

A composite body of the described character is illustrated in Figure 1 of the drawing wherein reference numeral 10 denotes the layer of titanium, and 11 is the layer of titanium carbide which extends continuously into the pores of the adjoining graphite layer 12, the further removed portions of which are unimpregnated and free from titanium carbide. This composition or composite body embodies the principles of the invention in their broadest aspects and is the basic material of the present invention. It is capable of various modifications and is adapted to many different practical applications, depending on the relative thickness of the various layers, some of which may be completely absent. For example, a graphite or carbon layer or body impregnated with titanium carbide, such as is shown at 14 in Figure 2, has greatly increased mechanical strength, decreased porosity and increased resistance to oxidation. Articles or structural parts made from graphite impregnated with titanium

carbide in the described manner are highly resistant to attack by combustion gases at temperatures up to 2200° F. and may be used for apparatus exposed to such temperatures.

According to a modification of the invention, a composite body of the described general character is formed by melting titanium in contact with dense graphite in vacuum and allowing the contact to persist for only a few minutes. There is obtained a composite body of the type shown in Figure 1 and the impregnated (and unimpregnated) graphite may be removed by making the said body an anode in dilute sulphuric acid bath, and passing a current in excess of 50 amperes per square foot anode surface through said bath. In this way, the graphite is removed from the surface of the composite body and the result is a layer of titanium completely covered with a roughened surface of titanium carbide. In preparing this composite material, the titanium is preferably melted between two graphite layers so that both sides of the titanium layer will be completely covered with titanium carbide. The titanium layer may be quite thin, as molten titanium wets graphite and will be drawn by capillarity into the smallest crevices. Titanium melted in a graphite crucible has been found to flow upward into spaces between hot graphite plates several inches high and $\frac{1}{32}$'' thick.

A composite body of the described character and comprising a layer or core 15 of titanium and titanium carbide 16 covering the surface thereof is shown in Figure 3 of the drawing. This material has outstanding properties as an anode for electrochemical oxidation. An electrode of titanium coated with titanium carbide in the described manner shows none of the tendency to form anodic films characteristic of titanium. It is unattacked by sulphuric acid or sulphates when used as an anode and by concentrated hydrochloric acid, unless the anode current density exceeds 100 amperes per square foot.

The titanium carbide coated titanium electrodes of the invention have been found particularly useful in making electrolytic manganese dioxide from manganese sulphate solutions containing sulphuric acid. Heretofore, graphite electrodes were employed for this purpose, but their use restricted the acidity and the current density that could be used. While it was known that both the process and the product could be improved by using platinum anodes, the cost of such anodes was prohibitive. The anodes of the present invention have been found to be in every way equivalent to platinum anodes for this purpose.

According to another modified embodiment of the invention, the composite body comprising titanium, titanium carbide, graphite impregnated with titanium carbide and unimpregnated or excess graphite is subjected to a treatment removing the excess graphite thereby providing an electrode having a surface composed of graphite that is fully impregnated with titanium carbide. If such an electrode is made the anode in dilute sulphuric acid and a direct current of 100–500 amperes per square foot passed between this anode and any inert cathode, the anode will be ennobled. An electrode prepared in this way may be used as the positive electrode of a primary cell, such as a conventional LeClanche cell and provides important advantages, such as a substantial increase in the electromotive force of the cell. Thus, while with a conventional carbon electrode the electromotive force of the cell is about 1.5 volts, with the ennobled electrode of the invention the electromotive force of the cell will be from 1.8 to 2.4 volts.

An electrode of the described character is illustrated in Figure 4 where reference numeral 17 denotes a layer or core of metallic titanium and numeral 18 denotes the carbon or graphite layer or layers impregnated with titanium carbide.

A further modification of the invention contemplates the preparation of a brush or sliding contactor for commutators, and the like, by removal of the unimpregnated or excess graphite from the titanium-titanium carbide-graphite composition by mild abrasion. Although the resistance to abrasion increases sharply as the impregnated portion of the graphite is reached, the low friction characteristic of a graphite surface is in a great measure retained. A fixed contact of high electrical conductivity to the titanium impregnated graphite can be made by melting or spraying copper on one surface thereof.

Titanium-impregnated carbon or graphite anodes of the described character are useful in space discharge of all types, such as in gas and high vacuum tubes, including rectifying tubes.

In order that those skilled in the art may have a better understanding of the invention, the following illustrative example may be given of the preferred method of preparing the titanium-titanium carbide-graphite composition which is the basic material contemplated by the present invention.

Referring now more particularly to Figure 5 of the drawing, reference numeral 20 denotes a vacuum melting furnace which is electrically heated by a heater element in the form of a split graphite cylinder 21 surrounding graphite crucible 24 and is connected to a vacuum pump (not shown) through a conduit 22. Metallic titanium in the form of chips prepared by the method of Kroll Patent 2,205,854 is pressed into compact masses 23 and these are placed in graphite crucible 24 in the upper portion of the furnace. Crucible 24 is provided with a small aperture 25 at the bottom so that when the titanium melts, it will flow from the crucible into a mold 26 in the lower portion of the furnace which gives the desired shape of the titanium-titanium carbide-graphite composition. The mold 26 is accordingly made of graphite and is heated to a temperature determined by the extent of impregnation of the graphite desired. The higher the temperature of the mold, the greater will be the impregnation. In the simplest case, the mold may take the form of a thin slit in a graphite block, as is shown at 27 in Figure 5. When the titanium 28 has been cast in this slit, the excess graphite beyond the zone of impregnation may be removed mechanically and the resulting strip of titanium coated on all sides with titanium carbide and graphite impregnated with titanium carbide is ready for further treatment to produce a positive electrode of a primary cell or for removal of the graphite to form an anode for an electrolytic manganese dioxide cell.

This procedure for producing the composite bodies of the invention is further illustrated in Figure 6 in which 26 is a block of graphite with a slit 27 therein constituting a mold and 28 is the consolidated body of titanium in said slit. Upon removal of the excess graphite along dotted lines 29 and 30, the composite body shown in Figure 7 is obtained, comprising layers of metallic titanium 28, titanium carbide 31 and graph-

ite impregnated with titanium carbide 32. This composite body may then be subjected to one of the further treatments disclosed more fully in the foregoing.

When it is desired to prepare only graphite impregnated with titanium carbide, a simple and inexpensive procedure is to melt titanium in a graphite crucible in a vacuum melting furnace and rely on the impregnation of the walls of such crucible when the titanium is melted. Thus, in a practical case, a generally cylindrical graphite crucible was provided having a diameter of 1½", a height of 3" and a wall thickness of ¼", with a small aperture in the bottom thereof. Titanium was melted in this crucible and allowed to flow into a mold, much in the same way as this is illustrated in Figure 5. The crucible walls were found to be uniformly and completely impregnated with titanium carbide. A cylindrical electrode suitable for a primary cell was made by removing the lower portion of the crucible.

This method is further illustrated in Figures 8 and 9. Figure 8 is a vertical sectional view of the carbide-impregnated graphite crucible 24 with a small aperture 25 in the bottom thereof. Upon cutting off the bottom portion of the crucible along dotted line 34, the carbide-impregnated graphite electrode shown in Figure 9 in the form of a cylindrical shell is obtained.

While the methods of manufacture described in the foregoing are the preferred ones, other methods have been used with success in producing the compositions of the invention. Thus, powdered titanium can be mixed with powdered carbon and the mixture compacted by pressure and heated to a temperature from 1500° C. to 2000° C. to form a carbon-titanium carbide mixture which can be used for the purposes described in this application. Likewise, metallic titanium can be heated in contact with carbon to a temperature just below the melting point of titanium to form a layer of titanium carbide on metallic titanium and the composition so formed can be used for the purposes herein described.

It has been found that for the purposes of the invention alloys of titanium containing at least 90% titanium can be used in place of pure titanium. Such alloys may in fact be advantageous because of their lower melting point. Examples of alloying constituents which may be used are iron, cobalt, nickel, chromium, manganese, molybdenum, tungsten, aluminum, beryllium and zirconium. The amounts of oxygen, nitrogen or carbon introduced into the titanium or its alloys by the heating step of this invention do not change the properties of the composition produced.

While the present invention, as to its objects and advantages, has been described herein as carried out in specific embodiments thereof, it is not desired to be limited thereby but it is intended to cover the invention broadly within the spirit and scope of the appended claim.

What is claimed is:

An electrode for use in electrochemical oxidation apparatus adapted to convert electrolytic manganese dioxide from manganese sulphate solutions containing sulphuric acid, said electrode being fabricated of the elements titanium, titanium carbide and carbon, said titanium forming a central core for said electrode, the outside surface of said core being attached to an exposed carbon layer impregnated with titanium carbide throughout, the percentage of carbon in said layer increasing in extent from the titanium core toward the surface of said impregnated layer, said electrode being characterized as capable of handling current densities of up to 100 amperes per square foot and resisting attack by sulphuric acid and sulphates.

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