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3,547,600

COMPOSITE ELECTRODE HAVING A BASE OF TITANIUM OR COLUMBIUM, AN INTERMEDIATE LAYER OF TANTALUM OR COLUMBIUM AND AN OUTER LAYER OF PLATINUM GROUP METALS

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7 Claims

ABSTRACT OF THE DISCLOSURE

Three component electrode having enhanced resistance to high voltage damage, particularly in chlorinating hypochlorinating, and similar electrolytic process, said electrode comprising a heavy substrate selected from the group consisting of titanium and columbium having thermoelectrically bonded thereto an intermediate layer about .0003 to .01 inch thick of a metal selected from the group consisting of tantalum and columbium and higher melting than the metal of said substrate, and an outer layer about .0003 to .005 inch thick of a platinum metal selected from the group consisting of platinum, rhodium, iridium, ruthenium and alloys thereof, and having a melting point lower than the metal of said intermediate layer. the thermoelectric bonding of said metal layers to the substrate being effected under sufficient thermoelectric heat and pressure to cause visible surface deformation of said substrate and intimate adherence of said intermediate and outer metal layer to the thus deformed surfaces of the substrate.

A preferred general purpose electrode has a titanium substrate, an intermediate layer of columbium or tantalum and an outer layer of a platinum metal. For unusually high voltage operation the substrate can be columbium, the intermediate layer tantalum and the outer layer a platinum metal.

BACKGROUND OF THE INVENTION

In the electrolysis of salt solution, particularly in chlorinating and hypochlorinating processes, considerable difficulty has been experienced in providing electrodes which will perform effectively for extended periods of time. By way of illustration in the chlorinating of swimming pools and the like it is desirable that electrodes should perform satisfactorily for a period of 3 to 5 years, but most electrodes used for this purpose in the past have lost efficiency or broken down completely in less than a year of operation.

Materials which are most advantageous in electrode construction both from the standpoint of chemical resistance and electric conductivity are the metals of the platinum group including in particular platinum, rhodium, iridium, ruthenium and alloys thereof. These metals are so expensive, however, as to prevent their use as electrodes for most electrolytic processes except as such metals are applied as thin layers or foils to less expensive supporting materials.

Various methods have been used in the past in attempts to suitably coat a substrate, such as tantalum, niobium, titanium, and alloys thereof, with metals of the platinum group, but with varying degrees of success and practicability. United States Pat. No. 2,719,797, for example, discloses chemical decomposition or electrolysis to form thin deposits of platinum metal in conjunction with heating to effect a bond with the substrate. These methods, however, tend to produce uneven or incomplete coatings of

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the platinum metal, and there is a substantial tendency for the heat treatment to modify the platinum metal composition and its electric conductivity, thereby reducing its effectiveness as an anode surface material.

It is pointed out in said United States Pat. No. 2,719,797 that "attempts to cover the tantalum strip with a platinum metal foil to hold the metals together, as by sweating, rolling or hammering, have proved to be unsatisfactory because the platinum metal foil is held to the tantalum only by mechanical contacts which is not sufficient to permit its use as an anode."

In applicants' copending application Ser. No. 520,596, filed Jan. 14, 1966 which issued as U.S. Pat. 3,443,055 on May 6, 1969, there is disclosed a method for bonding platinum metals to substrates such as tantalum, titanium and niobium (also known as columbium) under the influence of pressure and locally generated thermoelectric heat which produces electrodes that are far superior to previously available electrodes.

The improved electrodes as disclosed in said copending application comprises a laminated body of platinum metal foil bonded to a compatible metal substrate which is highly resistant to electrolytic oxidation, the bonding being effected by applying along a line of contact between a small diameter cylindrical member of hard conductive metal, rotatable in a massive electric conductor, in engagement with said foil, and a second massive electric conductor in engagement with said substrate, a pressure of about 10 to 300 pounds per linear inch, and an electric current below 12 volts at an amperage to provide at least 3 kva. per linear inch of said line of contact, while advancing said small diameter cylindrical member in a direction perpendicular to said line of contact at a rate to provide a bonding heat sufficient to soften, without melting, the substrate surface.

The platinum metal can be platinum, rhodium, iridium or ruthenium or alloys thereof; the substrate metal can be tantalum, titanium, niobium or alloys thereof; and the bonding is preferably effected at a pressure of 50 to 150 pounds per linear inch, using current of 0.1 to 5 volts at an amperage to provide 7 to 100 kva. per linear inch.

Preparing electrodes according to the method above described requires extreme precision in the pressure and rate of feed applied to the small diameter cylindrical member which forms the line of electrical contact with the workpieces. Insufficient pressure or too rapid advance of the cylindrical member can result in incomplete or discontinuous bonding of the platinum metal foil to the substrate, and too slow or uneven advance of the cylindrical member can cause rupture or burn-through of the foil. The latter type of damage can usually be detected by visual inspection and remedied by spot patching with additional foil applied by the same method. The incomplete or discontinuous bonding of the foil to the substrate is a more serious problem since it is difficult to detect by inspection.

It has been observed with numerous electrodes in the field that such incomplete or discontinuous bonding does not interfere with performance of an electrode, so long as the overlying layer of platinum metal remains sound and free of pores or microscopic breaks which might permit electrolyte to reach the substrate. When such break does occur, however, the entire area of incomplete bonding can rapidly be stripped of the platinum metal foil. If the area is small and the electrode is operating at a low voltage such as 6 to 8 volts the damage may not seriously impair the efficiency of the electrode, and electrodes with slight damage of this sort have been continued in use successfully for many months. If more than about 5% of the electrode surface is thus damaged its efficiency may be sufficiently reduced to warrant replacement. If the voltage at which the electrode is operated is appre-

ciably above 6 to 8 volts, however, any such rupture of an unbonded portion of the platinum metal can lead to erosion of the surrounding soundly bonded areas with progressive destruction of the entire electrode.

The problems due to incomplete or discontinuous bonding as above described have come into focus in extensive experiments which applicants have been conducting in which the thermoelectrically bonded electrodes have been operated at unusually high voltages for extended periods of time; and the surprising and unexpected results of such high voltage operation have indicated that there is a real need for eliminating the problem of latent failure due to incomplete or discontinuous bonding.

THE INVENTION

It has now been discovered, that the problems above described with electrodes having a platinum metal foil thermoelectrically bonded directly to a heavy metal substrate can be overcome by employing in addition to the platinum metal foil an intermediate metal foil which has a melting point appreciably higher than the platinum metal and the substrate. The method of bonding is generally similar to the method disclosed in said copending application differing somewhat therefrom in the optimum operating conditions as hereinafter described.

The key to the superior bonding attained with the three component system appears to be the use of an intermediate foil which has a substantially higher melting point than the platinum metal and the substrate. This provides a greater concentration of heat at a location to permit more effective surface softening of the substrate and assurance of intimate contacting of the superimposed metal surfaces throughout the length of the small cylindrical conductor as it is pressed against and rolled along the assemblage. This explanation of what is apparently taking place is based both on the intense orange glow which develops in the intermediate foil in alignment with the small cylindrical roller, and on the slight surface deformation of the bonded substrate and foils. In fact the path of the cylindrical roller on the assemblage tends to assume a slightly rippled contour, indicating that the localized heating is so instantaneous and sensitive that the softening of the substrate surface varies slightly in each cycle of the current supply.

The selection of metals to use in the substrate and foils should be made with reference to both the relative melting points and the type of use intended for the electrode. The following tabulation of melting points will serve as a guide:

	Metal	Approx. M.P., ° C.
Outer foil	{Platinum.....	1,773
	{Rhodium.....	1,966
	{Iridium.....	2,450
	{Ruthenium....	2,450
Middle foil	{Columbium....	2,415
	{Tantalum.....	2,850
Substrate	{Titanium.....	1,725
	{Columbium....	2,415

Bearing in mind that the middle foil should have a higher melting point than the outer foil and substrate it follows that if the substrate is titanium, the middle foil can be either columbium or tantalum; but if the substrate is columbium the middle foil will be tantalum. Also, if the middle foil is columbium, iridium and ruthenium should not be employed as the outer foil except as lower melting alloy forms.

In terms of intended use of the electrode an important factor is the voltage to be employed. Titanium can withstand only about 7 to 10 volts before showing signs of breakdown. Columbium on the other hand, can withstand up to about 45 volts and tantalum about 130 volts. Thus if an electrode is intended for operation in the 10 to 45 volt range a middle foil of columbium over a titanium substrate provides reasonable protection for the sub-

strate in the event of damage to the platinum metal exposing portions of the middle foil. For operation at voltages above about 45 volts such protection would best be provided by switching to a tantalum middle foil, and suitably also switching to columbium as the substrate.

The equipment employed in assembling the new electrodes is the same as that described in said pending application. The substrate can rest on a large massive conductor suitably in the form of a heavy plate of copper or highly conductive harder copper alloys. A moveable massive conductor grooved to receive a small diameter cylindrical roller of a hard conductive metal, such as tungsten, tungsten carbide, alloys of tungsten carbide, and stainless steel, is arranged above the first massive conductor in a manner to apply downward force against superimposed substrate and foils as the cylindrical roller is rotated to advance it over the superimposed workpiece in a direction perpendicular to its axis. The cylindrical roller can be of a length to traverse the full width of the electrode substrate or it can have a portion of enlarged diameter (fitting within a recess in the upper massive conductor) which provides a line of contact substantially shorter than the width of the electrode, requiring a number of passes to fully bond the superimposed foils to the substrate.

In a large scale adaptation of the method the flat bed massive conductor can be replaced, as disclosed in said pending application, with a large diameter roller, driven in synchronism with the small diameter roller, and having a diameter of the order of 10 to 20 times the diameter of the small diameter roller.

The operating conditions for assembling the three part electrode are somewhat more severe than those described in said pending application for laminating platinum metal foil directly to the substrate. The pressure applied should be about 600 to 3000 pounds and preferably about 840 to 1440 pounds per linear inch of contact between the small diameter cylinder (or enlarged portion thereof) and the superimposed foils and substrate; and the roller is rotated to advance the line of contact about 12 to 36 inches per minute. The applied voltage should be less than 10 volts, and suitably in the 0.5 to 5 volt range, with the applied current providing at least 30 and suitably 40 to 100 kva. per linear inch of contact by the small diameter roller (or enlarged portion thereof)—when using relatively thin substrate and foils. As the thicknesses of substrate and foils, and particularly the intermediate foil, are increased, the kva. can be increased to as much as about 500 kva. per linear inch.

It is important that the applied pressure and the speed of rotation of the small diameter roller advancing the same over the superimposed workpieces be maintained essentially constant, and that the electric current be turned on and off while the pressure is applied and the roller is in motion. There is no harm in going over a previously bonded area provided these limitations are adhered to; in fact when using a roller with an enlarged portion which contacts only part of the width of the electrode substrate it is important to overlap the previously bonded portion slightly when making the next pass in order to assure overall bonding of the superimposed foils. Any stopping of the forward movement of the roller while the current is on must be avoided, as this may cause a burn-through of one or both of the superimposed foils.

The substrate metal can be of any desired thickness to provide the desired rigidity in the electrode. For electrodes 2 to 3 inches wide and 6 to 12 inches long a thickness of about .03 to .25 inch is generally suitable. The middle foil is about .0003 to .01 inch and preferably about .001 to .0015 inch thick; and the outer platinum metal foil is about .0003 to .005 inch and preferably about .0003 to .0006 inch thick.

The following examples will serve to more fully demonstrate how typical electrodes in accordance with the present invention are assembled, but it is to be under-

stood that these examples are given by way of illustration and not of limitation:

Example I

Electrodes are prepared by bonding to flat sheets of titanium measuring 2 inches by 6 inches by .06 inch thick an intermediate foil 0.0015" thick of tantalum and an outer foil 0.0005" thick of platinum. In the bonding operation the titanium plate is placed on a large copper alloy bed providing one terminal of an electrical circuit. A hand held copper electrode forming the outer side of said current has a transverse groove in the lower end thereof which receives a rotatable tungsten carbide cylinder about 0.5 inch in diameter having a central enlargement about 0.75 inch in diameter, and having an axial length about 0.25 inch, with a slightly rounded surface contour. The end of the cylinder is provided with an offset crank to facilitate controlled rotation along the foils as the same slidably rotates in the hand held electrode.

While applying a downward pressure of about 80 pounds to the superimposed foils and titanium plate (providing about 800 pounds per linear inch at the line of contact between the roller enlargement and the platinum foil) the crank is turned at a rate to advance the line of contact at the rate of about 12 inches per minute. With the pressure thus applied and motion initiated a foot switch is actuated to apply current between the conductors from a 2.5 volt power source capable of delivering 5000 amperes. This amount of power provides about 125 kva. per linear inch along the line of contact of the roller enlargement with the platinum foil. When approaching the end of the titanium plate the foot switch is released to cut off the power supply and only then is the application of pressure and rotation of the roller terminated.

As observed from the side the heat generated by the applied current provides a bright orange glow, apparently concentrated primarily in the tantalum foil in a small area directly aligned with the line of contact established by the roller enlargement.

The steps above described are repeated along a second path in which the line of contact with the roller enlargement slightly overlaps the first path, and the sequence of steps is repeated a number of times until the superimposed foils have been bonded to substantially the entire area of the titanium plate.

Overhanging edges of the foils are cut off slightly beyond the edges of the titanium plates, folded around the titanium plate, and bonded to the reverse side thereof by inverting the assemblage on the conductor base and repeating the bonding procedure along the folded over portions of the foils.

Terminal posts are then welded to the reverse side of the titanium plate, and the reverse side and edges of the assemblage are encased in a resistant resin, suitably a polyacrylic resin such as methyl methacrylate polymer to insulate and protect portions of the assemblage not covered by the superimposed foils.

In the paths made in the bonding operation there are slightly visible ripples quite uniformly spaced along each path which are caused by fluctuations in the alternating current supply. There are also slight ridges at the overlap between successive bonded paths. When an electrode is torn apart to separate the foils from the substrate these ridges and ripples appear in the substrate in exact conformance with the surface appearance indicating that a progressive softening and displacement of the surface metal which provides the desirable overall bonding of the superimposed foils to the substrate.

Electrodes prepared as above described are extremely durable in chlorinating operations at 10 to 40 volts, and current densities ranging from a trace to 5 amps/sq. in. of electrode surface, and such electrodes have an estimated useful life, based on 10 to 12 hours per day of operation, in excess of five years.

At these voltages the electrodes have operated successfully for long extended periods at current densities as high as 30 amps/sq. in. of electrode surface. Furthermore the electrodes have shown remarkable stability at potentials as high as 220 volts and current density of the order of 1 amp/sq. in. of electrode surface.

In the foregoing example it is to be understood that tantalum and platinum metal foils can be bonded to the reverse side of the electrode, if desired, by repeating the procedural steps described with the previously bonded surface bearing against the copper alloy bed. For many uses and adaptations of the electrodes, however, such coating of the reverse side of the electrode is unnecessary and would be uneconomical in view of the cost of the foil materials.

The procedure as described in the foregoing example can readily be adopted to the bonding of substrate and foils of different thickness or different composition. In general the applied pressure and the kva. of current per linear inch should be increased as the thicknesses of the substrate and foils are increased, and decreased as these thicknesses are decreased. Alternatively, the amount of heat generated along the line of contact of the pressure roller with the assemblage can be increased or decreased by respectively slowing or increasing the rate of advance of the line of contact, while holding the applied current constant.

If the tantalum intermediate foil in the foregoing example is replaced by the same thickness foil of the lower melting columbium the same operating conditions will nevertheless apply. On the other hand, if the titanium substrate is replaced by the higher melting columbium somewhat higher current or slower advance of the line of contact of the pressure roller is required to provide the same degree of softening of the substrate surface.

Various changes and modifications in the three component bonded electrodes and the method for producing the same as herein disclosed may occur to those skilled in the art, and to the extent that such changes and modifications are embraced by the appended claims it is to be understood that they constitute part of the present invention.

We claim:

1. A three component electrode having enhanced resistance to voltage damage comprising a heavy substrate selected from the group consisting of titanium and columbium having thermoelectrically bonded thereto an intermediate layer about .0003 to .01 inch thick of a metal selected from the group consisting of tantalum and columbium and higher melting than the metal of said substrate, and an outer layer about .0003 to .005 inch thick of a platinum metal selected from the group consisting of platinum, rhodium, iridium, ruthenium and alloys thereof, and having a melting point lower than the metal of said intermediate layer, the thermoelectric bonding of said metal layers to the substrate being effected under sufficient thermoelectric heat and pressure to cause visible surface deformation of said substrate and intimate adherence of said intermediate and outer layers to the thus deformed surface of the substrate.

2. A three component electrode as defined in claim 1 wherein the intermediate foil is about .001 to .0015 inch thick and the platinum metal foil is about .0003 to .0006 inch thick.

3. A three component electrode as defined in claim 1 wherein the substrate is titanium and the intermediate layer is columbium.

4. A three component electrode as defined in claim 1 wherein the substrate is titanium and the intermediate layer is tantalum.

5. A three component electrode as defined in claim 1 wherein the substrate is columbium and the intermediate layer is tantalum.

6. A three component electrode as defined in claim 1 wherein the thermoelectric bonding is effected between

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a massive electrode supporting said substrate and a conductive roller electrode engaging said outer layer by applying a voltage below 10 volts at an amperage to provide at least 30 kva. per linear inch of conductive roller contact with the superimposed layers while applying a pressure of 600 to 3000 pounds per linear inch and advancing said line of contact at the rate of about 12 to 36 inches per minute.

7. A three component electrode as defined in claim 1 wherein the thermoelectric bonding is effected between a massive electrode supporting said substrate and a conductive roller electrode engaging said outer layer by applying a voltage in the 0.5 to 5 volt range at an amperage to provide 40 to 100 kva. per linear inch of conductive roller contact with the superimposed layers while applying a

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pressure of about 840 to 1440 pounds per linear inch and advancing said line of contact at the rate of about 12 to 36 inches per minute.

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