United States Patent Office 3,129,163 Patented Apr. 14, 1964

3,129,163

ANODE FOR ELECTROLYTIC CELL

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No Drawing. Filed Dec. 23, 1960, Ser. No. 77,826
7 Claims. (Cl. 204—290)

This invention relates to metallic electrodes for use in electrolysis processes and in particular to improved anodes for use in the electrolytic production of chlorine.

In the production of chlorine by the electrolysis of sodium chloride solution, anodes are sought which exhibit both good electrical and corrosion resistance characteristics. Graphite anodes are generally employed in the two types of cells currently used in the production of chlorine—the diaphragm cell and the mercury cathode cell.

Graphite, while electrically conductive and possessing a high degree of chemical resistance, is not altogether suitable for use as anodes in such cells. The graphite is subject to decomposition through oxidation, as well as subject to destruction by erosion. The resulting change in dimensions destroys the preset relationship between anode and cathode, increasing the distance between these electrodes and causing an increase in the voltage across the cell. Such variation in cell dimensions causes a decrease in the operating efficiency of the cell.

Other materials have been substituted for graphite in cell anodes. Platinum and many platinum alloys are quite satisfactory but too expensive for general use in the massive form.

In order to utilize the excellent electrical conductance characteristics of platinum and yet avoid the expense of providing solid platinum anodes, electrodes were long ago constructed which had a base or core of a chemically resistant metal such as tantalum, and an additional metallic part in intimate physical contact with the core which is composed of one or more of the platinum group metals, usually in the form of a platinum plating. The platinum metal surface serves as the effective current conductor to the electrolyte while the tantalum core serves as a satisfactory support for the platinum because it, like the platinum, is chemically resistant to the electrolyte. The chemical resistance of the tantalum support is due to an inert oxide film formed when the tantalum contacts the electrolyte. Unfortunately, this oxide film interferes with the formation of a lasting bond between the core metal and the platinum plating. The platinum plating, not being firmly bonded to its support, is thereby subjected to erosion whereby the area of platinum coating is diminished. Since only the platinum-plated area is an effective conductor in such anodes—the tantalum oxide film being highly nonconductive—the voltage requirements increase as the platinum-plated area diminishes due to erosion. These anodes must be replated, therefore, with the resulting loss of operating time and materials.

It has also been proposed that anodes for use in the electrolytic production of chlorine be composed of a titanium core with a platinum metal plating. Such anodes are similarly subject to the loss of platinum through erosion with the resulting decrease in cell efficiency.

It is the primary object of this invention, therefore, to provide an improved anode for use in electrolytic cells.

It is another object of this invention to provide materials for use as cores in such anodes, which material is capable of forming strongly adherent bonds with the platinum metal applied thereon.

It is also an object of this invention to provide materials for use as cores in such anodes, which material is strong and ductile and capable of being formed into thin sheet that will not buckle.

These and other advantages of the instant invention will be apparent from the following description and the appended claims.

These objects are achieved by providing an anode for use in an electrolytic bath, said anode having a core of base metal comprising an alloy containing from 4 to 30 percent by weight tungsten and the balance titanium, said core or base being at least partially coated with a metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, and alloys thereof.

Anodes made according to this invention exhibit less peeling and loss of the precious metal and show less tendency to buckle when employed in the form of thin sheets.

The tungsten-titanium alloy disclosed above for use in the core section is disclosed and claimed in co-pending application Serial No. 820,943, filed June 17, 1959, now abandoned.

The alloy is characterized in having a high degree of ductility after quenching from the beta field. The alloy may then be worked to bar, sheet, and other mill products by conventional techniques. These products can then be age-hardened to a high tensile strength while retaining adequate ductility. Anodes having a core fashioned from thin sheets of this alloy are strong and resistant to buckling.

The process for producing the age-hardened anode cores of this invention consists of a two-part heat treatment. The initial step consists of solution heat treating the alloy at temperatures within the beta field or alpha plus beta field and particularly at temperatures between 1325 and 1950° F. The alloy is then quenched from the solution heat treatment temperature to room temperature which results in a supersaturated structure. The alloy is then in a relatively soft and formable condition and can be worked into suitable anode shapes. The resulting products can be age-hardened at temperatures between 1100 and 1300° F. for from 1 to 4 hours to develop strength.

Table I shows the mechanical properties of several alloy compositions after solution heat treatment in the beta field (1740° F.) for one hour and water quenched.

TABLE I

Mechanical Properties After Solution Heat-Treatment

Alloy Composition Wt. Percent Tungsten	Yield Strength, lb./sq. In.	Tensile Strength, lb./sq. In.	Elongation in ½ In., Percent	Reduction in Area Percent	Vickers Hardness Number
7.9	86,700	105,800	22	59	247
11.8	97,600	115,400	26	72	242
12.8	103,700	150,000	25	60	324
13.3	69,700	112,400	26	72	236
17.8	71,100	137,800	30	60	294

The age hardening characteristics of the alloy are a function of the composition. Tungsten-titanium alloys containing up to 12 percent by weight tungsten exhibit a fully martensitic structure. Alloys containing from 12 to 23 percent tungsten consist of martensite plus retained beta structure. A 30 percent tungsten alloy consists entirely of retained beta structure. Upon aging of the alloy after solution heat treatment and quenching, the hardness increased significantly for alloys having a mini-

mum content of 4 percent and was extensive at higher tungsten contents.

In Table II the high strengths developed after aging are shown for several tungsten-titanium compositions.

TABLE II

Effect of Aging on Mechanical Properties

Alloy Composition, Wt. Percent Tungsten	Aging treatment		Yield Strength, lbs/sq. Inch	Tensile Strength, lbs/sq. Inch	Elongation in ½ Inch, Percent	Reduction of Area, Percent	Vickers Hardness Number
	Temperature,° F.	Time, Hours					
7.9	1,110	1	162,400	168,200	4	5	337
11.8	1,110	1	136,800	145,900	8	26	289
12.8	1,200	4	209,700	215,400	2	3	
13.3	1,100	1	146,200	157,700	10	23	323
17.8	1,290	1	178,900	186,200	4	5	369

Prior to the aging treatment shown in the table, these alloys were solution heat treated in the beta field (1740° F.) for one hour and water-quenched.

After the alloy has been formed into a suitable electrode shape and aged, it is coated with one of the conductive metals ruthenium, rhodium, palladium, osmium, iridium, platinum, and gold, or alloys of these metals. This coating may be applied by chemical deposition, or by electrodeposition such as with a Pfanhauser bath, or other means. The coating should be thin and uniform but need not be continuous for all applications.

An anode so constructed of the alloy described and coated with platinum or one of the platinum group metals will operate more efficiently as an anode in chlorine production than a similar anode composed of a pure titanium base coated with platinum. The superiority of the anodes of this invention in this regard is believed to be due to the increased adherency of the platinum film to the titanium-tungsten alloy base over the adherency of platinum to pure titanium, there being less erosion of the platinum from the anode of this invention.

As an example of the practice of the invention, a titanium-tungsten alloy consisting essentially of 15 percent tungsten and the balance titanium was fabricated by the processes described above into a rectangular bar. An anode was then prepared by platinum coating the bar in a hot Pfanhauser plating bath for about 90 seconds at 10 ma./cm.^{2} to give a plating about 4 microinches thick. This plated bar was made the anode in a 2.5 molar sodium chloride solution at room temperature. Electrolysis was carried out at 150 ma./cm.^{2} for 45 minutes without any attack or erosion of the coating. The platinum coating was then scratched with a file to provide discontinuities and the current continued for 2 more hours. There was still no attack. The current was thereupon raised to 200 ma./cm.^{2} for another 85 minutes without any attack.

Concentrated hydrochloric acid was added to the solution so that the current rose to 225 ma./cm.^{2}, but after 25 minutes there was still no attack. A plain titanium-platinum coated anode would undergo considerable attack or erosion under these conditions.

Another set of electrodes were prepared of similar dimensions and surface area, one having a base composed of the 15 percent tungsten-balance titanium alloy described above and the other having a base of substantially pure titanium. These electrodes were given similar platinum coatings and used as anodes in a modified Gibbs caustic-chlorine diaphragm test cell. These tests were conducted for an extended period of 75 days with the results shown in Table III. The increase in terminal voltage is an indication of the decreased conductivity of the anode.

TABLE III

Anode Efficiency

Days of Continuous Operation	Terminal Voltage, volts	
	Platinum coated titanium	Platinum coated titanium-15% tungsten
20	3.52	3.54
30	3.54	3.54
40	3.59	3.49
50	3.76	3.63
60	3.68	3.60
70	3.68	3.49
75	3.74	3.50

It is seen from the results of Table III that after 30 days of operation the titanium-15% tungsten-platinum plated anode of this invention exhibited higher conductance and a lower terminal voltage requirement than the plain titanium-platinum plated anode. The superior conductivity characteristics of this electrode allows for a considerable saving in power needs, as well as a reduction in the amount of time wasted reconditioning plain titanium-platinum plated anodes from which the platinum coating has eroded.

It is to be understood that anodes of any configuration may be made from this alloy. Bar electrodes or sheet, wire, mesh, or grid type electrodes are easily made according to the processes described above with this ductile alloy. The sheet and grid electrode have the advantage of strength and freedom from buckling required in a thin sheet material.

What is claimed is:

1. An anode for use in electrolytic cells comprising a base of an alloy consisting essentially of from 4 to 30% by weight tungsten and the balance substantially all titanium and incidental impurities, said anode base being at least partially coated with a metallic material selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and gold.

2. An anode for use in electrolytic cells comprising a base of an alloy consisting essentially of about 15 percent by weight tungsten and the balance substantially all titanium and incidental impurities, said anode base being at least partially coated with a metallic material selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and gold.

3. An anode for use in electrolytic cells comprising a base of an alloy consisting essentially of about 15 percent by weight tungsten and the balance substantially

all titanium and incidental impurities, said anode base being at least partially coated with platinum.

4. An anode for use in electrolytic cells comprising a base of an alloy consisting essentially of from 4 to 30 percent by weight tungsten and the balance substantially all titanium and incidental impurities, said anode base being at least partially coated with platinum.

5. A process for producing a strong, buckling-resistant anode for use in electrolytic cells comprising preparing an alloy consisting essentially of from 4 to 30 percent by weight tungsten and the balance substantially all titanium and incidental impurities, solution heat treating said alloy at a temperature between 1325 and 1950° F., thereupon forming said alloy into a desired anode form and aging said alloy anode form at a temperature between 1100 and 1300° F. for from 1 to 4 hours, and at least partially coating said anode form with a metallic material selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and gold.

6. A process for producing a strong, buckling-resistant anode for use in electrolytic cells comprising preparing an alloy consisting essentially about 15 percent by weight tungsten and the balance substantially all titanium and incidental impurities, solution heat treating said alloy at

a temperature between 1325 and 1950° F. thereupon forming said alloy into a desired anode form and aging said alloy anode form at a temperature between 1100 and 1300° F. for from 1 to 4 hours, and at least partially coating said anode form with a metallic material selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, and gold.

7. A process for producing a strong, buckling-resistant anode for use in electrolytic cells comprising preparing an alloy consisting essentially of about 15 percent by weight tungsten and the balance substantially all titanium and incidental impurities, solution heat treating at a temperature between 1325 and 1950° F., thereupon forming said alloy into a desired anode forming and aging the alloy anode form at a temperature between 1100 and 1300° F. for from 1 to 4 hours, and at least partially coating said anode form with platinum.

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