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[54] PROCESS AND ELECTROLYTE FOR APPLYING BARRIER LAYER ANODIC COATINGS

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[52] **U.S. Cl.** .... **204/33,** 204/56 R, 204/58
[51] **Int. Cl.** **C23b 9/02,** C23b 11/02
[58] **Field of Search** .... 204/56 R, 58, 33

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[57] ABSTRACT

Various metals may be anodized, and preferably barrier anodized, by anodizing the metal in an electrolyte comprising quaternary ammonium compound having a complex metal anion in a solvent containing water and a polar, water soluble organic material.

10 Claims, 2 Drawing Figures

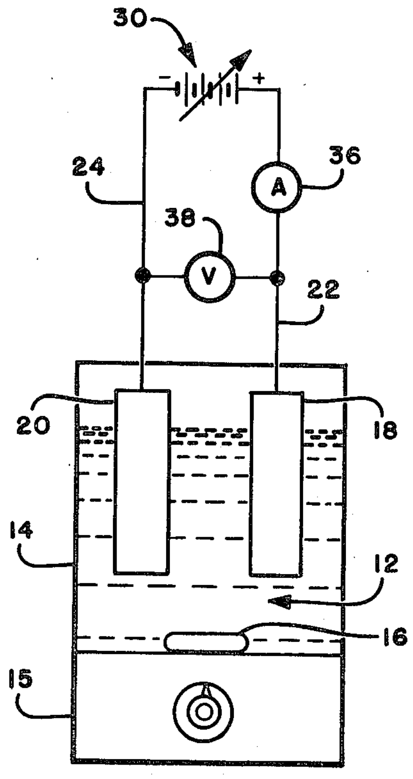


FIG. 1

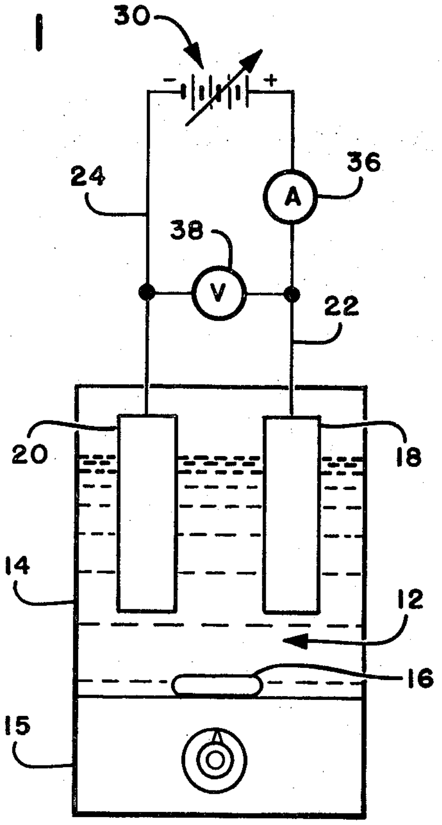
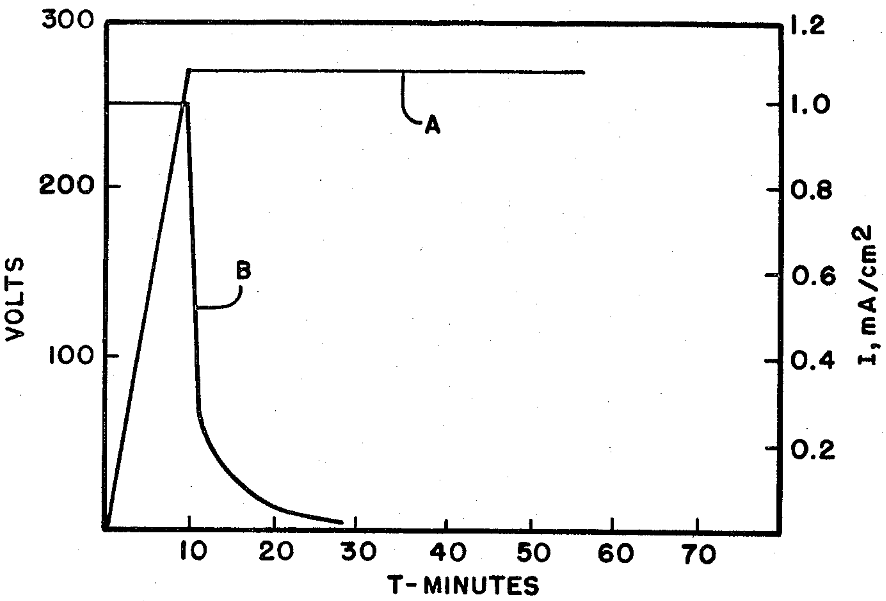

30
-
+
24
36
A
38
V
22
20
18
14
12
16
15

FIG. 2


300
200
100
VOLTS
1.2
1.0
0.8
0.6
0.4
0.2
I, mA/cm2
A
B
10
20
30
40
50
60
70
T-MINUTES

PROCESS AND ELECTROLYTE FOR APPLYING BARRIER LAYER ANODIC COATINGS

BACKGROUND OF INVENTION

The invention relates to applying anodic, and preferably barrier anodic films or coatings to various metals, and the electrolyte used to effect the anodizing process.

The use of barrier anodic coatings for capacitors is generally known. Barrier anodization generally refers to anodic coatings that are essentially pore free and are generally of the order of about 10^{-7} meters in thickness whereas conventional anodic coatings are about 10^{-5} meters in thickness. Barrier anodization using prior art processes and electrolytes has been successful in barrier anodizing high purity aluminum but has generally been unsuccessful in attempting to barrier anodize either aluminum alloys or large areas of pure aluminum with pore free anodized films.

Known barrier anodizing electrolytes for aluminum such as (a) aqueous boric acid-borax solutions, (b) aqueous or semi-aqueous solutions containing citrate or tartrate ions, and (c) solutions of ammonium pentaborate decahydrate in ethylene glycol may be suitable for high purity aluminum, but are generally unsuitable for barrier anodizing of aluminum alloys such as 7075 aluminum. Alluminum alloys referred to herein are designated by the four-digit designation system established by the Aluminum Association and generally known in the art.

SUMMARY OF INVENTION

In view of the above, it is an object of this invention to provide a novel electrolyte suitable for anodizing aluminum and its alloys.

It is a further object of this invention to provide a novel barrier anodizing electrolyte suitable for barrier anodizing various metals such as tantalum, tungsten, niobium, titanium, beryllium, and uranium and alloys thereof.

It is a further object of this invention to provide a novel barrier anodizing electrolyte suitable for barrier anodizing large surfaces.

It is a further object of this invention to provide a novel barrier anodizing electrolyte which comprises a solvent having water and organic, water soluble liquid or material, and having dissolved therein a solute in the form of a metal-containing quaternary ammonium compound.

Various other objects and advantages will appear from the following description of the invention, and the most novel features will be particularly pointed out hereinafter in connected with the appended claims. It is to be understood that various changes in the details, materials, process steps and the like which are herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art without departing from the scope of the invention.

The invention comprises a novel anodizing, and especially barrier anodizing, electrolyte and the method for using this electrolyte, which electrolyte includes a quaternary ammonium compound having a compex metal anion dissolved in a solvent. Examples of metals which may be barrier anodized using this electrolyte include tantalum, tungsten, niobium, titanium beryllium, uranium, aluminum and alloys thereof.

DESCRIPTION OF DRAWING

FIG. 1 represents a electrical schematic for anodizing.

FIG. 2 illustrates current-voltage curves derived in barrier anodizing of pure aluminum.

DETAILED DESCRIPTION

FIG. 1 represents an electrical schematic of an anodizing apparatus which may be used with this invention. The electrolyte **12** described hereinbelow is disposed within a container **14** and may be stirred or agitated using a magnetic or the like stirrer **15** together with stirring means such as a plastic coated magnet **16**. The anode **18** and cathode **20** may be electrically connected by means of electrical conductors **22**, **24** to a power supply such as a variable voltage power supply **30**. Further, an ammeter **36** and a voltmeter **38** may be disposed in the circuit as shown in order to measure current flow through the circuit.

In using this invention, compounds having the general formula $(R_4N)(M_xO_yH_z)$ where R is an alkyl group generally containing from 1 to 4 carbon atoms, an aryl group, or a mixture of these to form the quaternary ammonium ion, O represents oxygen, H represents hydrogen, and M represents a metal such as niobium, tantalum, or titanium, and where the complex ion contains two or more atoms of metal. Compounds having this formula, such as tetramethylammonium niobate, tetramethylammonium titanate and tetramethylammonium tantalate, may be formed by reacting quaternary ammonium hydroxide with a metal alkoxide. It is believed that the following equation accurately represents the portion of a reaction that is pertinent to this invention, but the invention is not to be bound or restricted by this belief:

$$(CH_3)_4N(OH)+Nb(OR')_5 \rightarrow (CH_3)_4N(Nb_2O_6H)+\text{other products} \qquad (1)$$

or, in general

$$(R_4N)(OH)+M(OR')_n \rightarrow (R_4N)^+(M_xO_yH_z)^-+\text{other products} \qquad (2)$$

where R and R' may be alkyl or other organic groups containing from 1 to about 4 carbon atoms, n is the valence of the metal M, and the values of x, y, and z are dependent upon the value of n. M may be such as niobium, tantalum and titanium. It may be desirable to use a solution such as an about 25 weight percent quaternary ammonium hydroxide in alcohol to effect reaction 1 or 2. The metal alkoxide is then mixed and thereby reacted with the quaternary ammonium hydroxide to form the desired quaternary ammonium compound having a complex metal anion. This compound may be separated from the reaction products by precipitation with a less polar solvent such as acetone and subsequently separating by suitable processes such as filtration or decantation.

This compound is dissolved in a suitable solvent comprising water and a polar, water soluble organic liquid such as alcohol or ethylene glycol wherein the alcohol volume percent may be from about 1 to about 80 percent and preferably from about 20 to about 80, and wherein water constitutes the remainder. Typical alcohols which may be used are such as ethanol, methanol, propanol, etc. and which have the general formula ROH where R may contain 1 to about 3 carbon atoms. The amount of compound to be dissolved in the solvent is dependent upon many factors such as the extent of use to be made of the electrolyte, but may generally be from about 1 to about 10 grams per about 1,000 milliliters of solvent. It may be generally desirable to dissolve the compound in water and thereafter add a sufficient amount of a polar, water soluble organic material to bring to the desired volume. The resultant solution containing the dissolved compound is used as the barrier anodizing electrolyte and may be at a temperature of from about 0° to about 60°C, and preferably at from about 15° to about 25°C.

Using the above electrolyte, the materials to be anodized may be suitably cleaned or given a cleaning pretreatment through various means. For example, barrier anodic films can be formed on a 6,061 aluminum alloy after a cleaning pretreatment involving a detergent scrub and a vapor degreasing of the surface. Other cleaning procedures may involve cleaning the as-received surface with a suitable alkaline material, thereafter immersing the sample in an ultrasonic bath containing a suitable solvent such as trichloroethylene, and finally rinsing the sample with a suitable alcohol such as ethyl alcohol.

An alternative and preferred cleaning pretreatment sequence to be used for aluminum and aluminum alloys may involve degreasing the surface with a suitable solvent such as trichloroethylene, contacting the sample surface with an about 5 weight percent sodium hydroxide solution at a temperature of about 160°F for about 5 minutes, rinsing the etched sample with deionized water, contacting the sample with a 50 volume percent nitric acid solution which may be at about 90°F for about 5 minutes, thereafter rinsing again in deionized water, immersing the sample in a 20 volume percent sulfuric acid solution at about 80°F until such time as gas bubbles form on the aluminum surface such as about 5 minutes, and then applying an anodizing electrical current for about 90 seconds at a current density of 5 milliamps per square centimeter using a platinum, stainless steel or tantalum cathode, thereafter soaking the sample in said sulfuric acid bath for about 5 to 10 minutes after bubbles form on the aluminum surface, and thereafter rinsing with deionized water followed by a suitable rinse such as an alcohol rinse prior to contacting the barrier anodizing electrolyte.

The following table illustrates various properties of films which were formed on 6061 aluminum with the present invention. The electrolyte was prepared by dissolving 5 grams of tetramethylammonium niobate compound in about 500 milliliters of water and thereafter diluting to a volume of about 2,000 milliliters with ethyl alcohol. The samples to be anodized, which were about 3 inch squares (about 18 square inches surface area) of about 90 mil thickness of 6,061 aluminum alloy, were cleaned by scrubbing the surface with an alkaline solution, immersing thereafter in an ultrasonic bath containing trichloroethylene, and thereafter rinsing with ethyl alcohol:

Metal Compound in Electrolyte	Anodize Voltage	Cap.* (nf)	Dissip.** Factor	Leakage Current A/cm²		
Nb	300	294	.028	3.7×10^{-11}	at	2V
				9.5×10^{-8}	at	60V
Nb	500	—	—	4×10^{-11}	at	2V
				1.7×10^{-9}	at	90V
Ta	300	303	.021	6.5×10^{-10}	at	10V
Ta	500	—	—	3×10^{-12}	at	2V
				4.3×10^{-9}	at	100V
Ti	300	296	.014	5×10^{-11}	at	2V
				5×10^{-7}	at	20V
Ti	500	185	.015	2.4×10^{-10}	at	2V
				3.5×10^{-7}	at	20V

*Capacitance in nanofarads at 1000 hertz.

**Dissipation factor at 1000 hertz.

The cleaned samples were then immersed in the electrolyte and appropriately connected to electrical anodic leads. The cathode may be any suitable material such as platinum, tantalum, and stainless steel. The samples were anodized at a constant current of 2 milliamps per square centimeter until the voltage increased to a preset value as shown in the table. The voltage used is a function of the thickness of the anodic coating desired as described below. 300 and 500 volts were used as a preset value for these samples. When the desired voltage was reached, the voltage was held constant and the current was allowed to decrease to approximately 10 percent of its initial value. Current and voltage curves have been plotted against time and the results are similar to the FIG. 2 curves which were derived using a pure aluminum anode **18** and a platinum cathode **20.** Curve A represents voltage increase as a function of time to a preset voltage. Curve B represent current change as a function of time while the voltage increases to a preset value and is maintained constant thereafter.

Although the anodizing procedure employed maintained the current constant until a preset voltage was attained, it may be seen that the same coating may be achieved by retaining the voltage constant and varying the current, or combination of these where the current or the voltage may be retained constant in increments until the desired results are achieved.

Further, as recited above, although the voltage was held constant after the desired voltage was attained and the current was allowed to decrease to a percentage of the initial value, it may be desirable to remove the barrier anodized material immediately upon attaining the preset voltage. This is to be done at the discretion of the operator.

In the above anodizing step, a thick gelatinous film forms on the aluminum surface. When the samples are removed from the bath and air dried, this film flakes off leaving a barrier anodic film on the surface. When samples are reanodized after this process, the voltage goes immediately to the original anodizing voltage and the current rapidly falls to the final value obtained during the initial anodizing procedure. Reanodizing is not an essential part of this process but is merely illustrative of the effect upon voltage and current.

The thickness of the barrier anodic film has been shown to be proportional to voltage with film thickness in angstroms approximately equal to 12 times the final adodizing voltage. For example, in the cited table, the 300 V anodizing voltage yielded a thickness of about 3,600A and the 500 V setting yielded a thickness of about 6,000A. Film thicknesses of 6,500 A have also been applied to pure aluminum and aluminum alloys such as 6,061 Al and 7075 Al.

In one instance, a gold counter electrode was deposited over a 20 centimeter square area of the barrier anodic film obtained by the above process and tested. The above table illustrates the electrical properties deteremined on one set of samples.

This invention demonstrates that the novel electrolyte of this invention can be used to form barrier anodic films on materials which are not commonly amenable to prior art electrolytes, and the method for using this electrolyte. For example, other aluminum base metals which have been anodized include 5,457 Al, 7,075 Al, 4,043 Al and pure aluminum. Except for 4,043 Al which was not tested, these had leakage currents at 2 volts of about 4×10^{-11} amperes per square centimeter. Areas as large as 575 square inches of 6,061 Al have been barrier anodized at 500 V to a thickness of about 6,000A using this electrolyte and process.

Voltages used in barrier anodizing other metals using the process and electrolyte of this invention include uranium alloys — 400 volts, beryllium— 300 volts, tantalum — 300 volts, tungsten — 150 volts, niobium — 200 volts and titanium — 400 volts. These voltages are merely exemplary and could be larger or smaller depending upon film properties desired.

What is claimed is:

1. The method for forming an anodized, essentially porefree film on metals selected from the group consisting of niobium, tantalum, tungsten, titanium, beryllium, uranium, aluminum, and alloys thereof, comprising cleaning said metal, thereafter immersing said metal in an electrolyte comprising a quaternary ammonium compound having the general formula $(R_4N)(M_xO_yH_z)$ where R is selected from the group consisting of an alkyl group having from 1 to 4 carbon atoms, an aryl group and mixtures thereof, N is nitrogen, O is oxygen, H is hydrogen, and M is a metal selected from the group consisting of niobium, tantalum, and titanium, and x is at least two, said quaternary ammonium compound dissolved in a solvent of water and a polar, water soluble organic liquid selected from the group consisting of an alcohol having the general formula ROH where R is an alkyl group having from 1 to 3 carbon atoms, and ethylene glycol, attaching said metal to an electrical lead to make it an anode, applying current to said anode while in said electrolyte for a time sufficient to form said film, and thereafter removing said anodized metal from said electrolyte.

2. The method of claim **1** wherein said current is from about 0.1 to about 10.0 milliamps per square centimeter, said time in continued to attain a desired voltage proportional to desired film thickness, maintaining said attained voltage constant while continuing to pass said current, and discontinuing said current passage after said current value has decreased to about 10 percent of its original value.

3. The method of claim **2** wherein said metal is an aluminum based metal and said current is continued for times sufficient to form a film thickness in angstroms of about twelve times the predetermined voltage value.

4. The method of claim **1** wherein said current is continued for a time to form film thickness of equal to or less than about $10^{116\ 7}$ meters.

5. The method of claim **1** wherein said solvent comprises from about 1 to about 80 volume percent water and from about 99 to about 20 volume percent alcohol.

6. The method of claim **1** wherein said quaterenary ammonium compound comprises from about 1 to about 10 grams of said compound per liter of solvent.

7. The method of claim **1** wherein said quaternary ammonium compound is a reaction product of a quaternary alkyl ammonium hydroxide and a metal alkoxide.

8. The method of claim **1** wherein said quaternary ammonium compound is selected from the group consisting of tetramethylammonium niobate, tetramethylammonium titanate, tetramethylammonium tantalate.

9. The method of claim **1** wherein said metal comprises aluminum and its alloys, said cleaning comprises degreasing the metal, etching the surface by contacting said surface in an alkaline bath, rinsing said etched surface with deionized water, contacting said surface with an about 50 volume percent nitric acid solution to desmut said surface, rinsing said surface with deionized water, immersing said surface in an about 20 volume percent sulfuric acid solution, attaching an electrical lead to said metal to make it an anode, applying current to said anode for about 90 seconds, thereafter soaking said surface for from about 5 to about 10 minutes in said sulfuric acid bath, rinsing said surface with deionized water and rinsing said surface with an alcohol.

10. The method of claim **1** wherein said metal has a surface area of about 575 square inches, and said anodized film is formed on said surface area.

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