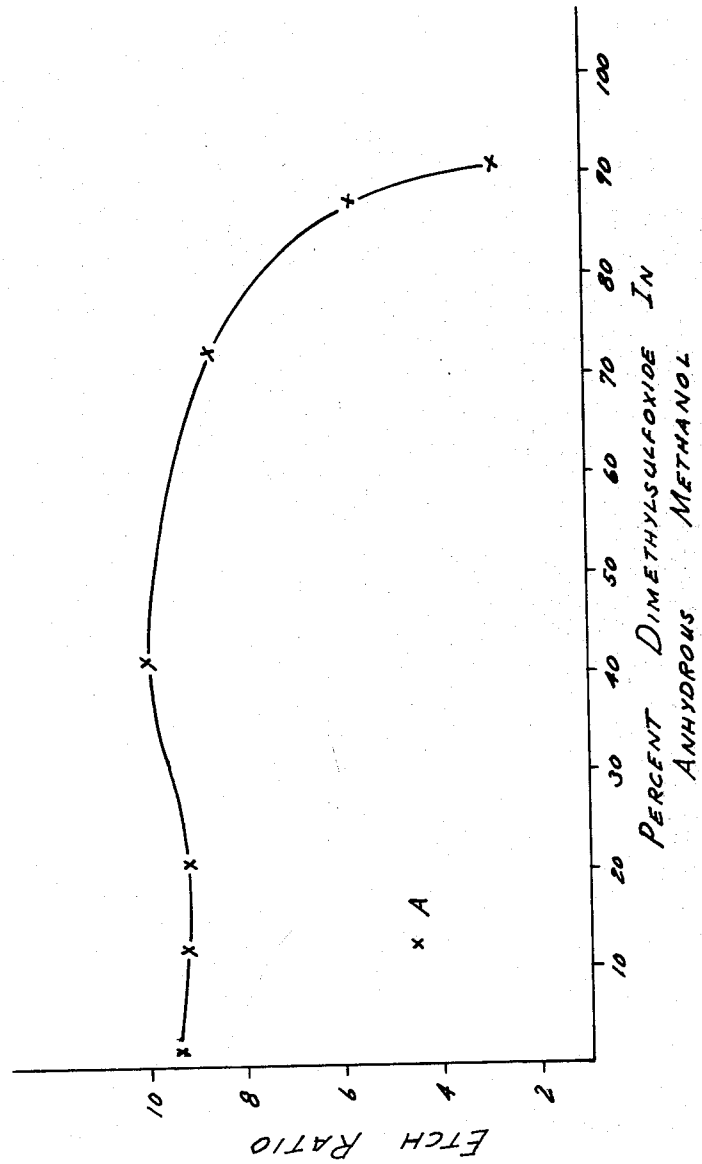
July 5, 1966 J. BURNHAM 3,259,475

ETCHED METAL VALVE SURFACES OF TANTALUM OR NIOBIUM OR TITANIUM

Original Filed Jan. 9, 1961 2 Sheets-Sheet 1

FIG. 1.



INVENTOR.
JOHN BURNHAM
BY Edward O'Brien
Attorneys

ETCHED METAL VALVE SURFACES OF TANTALUM OR NIOBIUM OR TITANIUM

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FIG. 2.

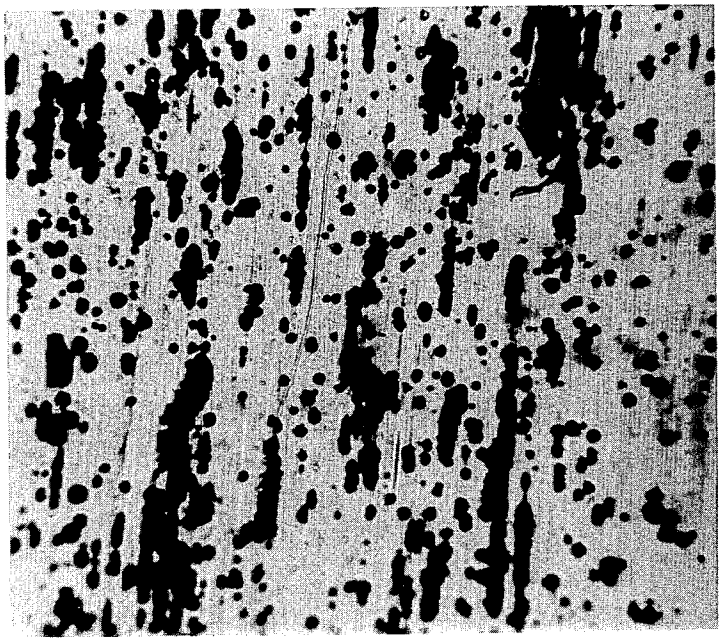


FIG. 3.

INVENTOR
JOHN BURNHAM
BY Donald J. O'Brien
ATTORNEY

United States Patent Office

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ETCHED METAL VALVE SURFACES OF TANTALUM OR NIOBIUM OR TITANIUM

John Burnham, 10960 Verano Road,
West Los Angeles, Calif.

Original application Jan. 9, 1961, Ser. No. 81,396, now Patent No. 3,190,822, dated June 22, 1965. Divided and this application May 3, 1965, Ser. No. 452,621
5 Claims. (Cl. 29—183)

This is a division of application Serial No. 81,396, filed January 9, 1961, now Patent No. 3,190,822.

This invention pertains to etched surfaces of inert valve metal electrodes.

In electrolytic capacitors valve metal electrodes are used because of the asymmetrical electrolytic characteristics of adherent oxide coated surfaces of such metals. It is established practice to etch such electrodes in order to increase their surface areas so as to make it possible to use relatively small electrodes in order to obtain relatively high capacitance ratings. The term "etch ratio" is commonly used in order to designate the proportionate amount by which the effective surface areas of an electrode is increased by etching.

It is not considered necessary to set forth in this specification the reasons why relatively inert valve metal electrodes, such as tantalum, niobium, and titanium electrodes are used in manufacturing electrolytic capacitors instead of electrodes formed of the relatively more reactive metal aluminum. Unfortunately inert valve metals as indicated above cannot be etched satisfactorily using the established types of processes for etching commonly employed with aluminum. As a consequence of this a great deal of research and development activity has been devoted to the etching of inert valve metals and in particular tantalum.

Such work has resulted in processes for electrolytic etching tantalum in various types of electrolytes such as, for example, aqueous hydrofluoric acid electrolytes and non-aqueous electrolytes in which solvents such as methanol or formamide contain inorganic ionogens. Such processes are considered to require "critical" concentration control within the electrolytes used in them. Frequently such concentrations are relatively difficult to achieve and maintain. It is considered that prior etching processes of these types for use with inert valve metals such as tantalum have not been successful in producing etched surfaces of a uniform, satisfactory character having high etch ratios.

An object of this invention is to provide etched surfaces on inert valve metals which are different from the etched surfaces provided on such metals by prior processes and which have comparatively high effective surface areas as indicated by etch ratio measurements.

A further object of this invention is to provide etched inert valve metal electrodes which are physically strong, which have comparatively high etch ratios and which may be easily created.

These and other objects of this invention as well as many specific advantages of it will be apparent to those skilled in the field of etching capacitor electrodes from a detailed consideration of the remainder of this specification including the appended claims and the accompanying drawings in which:

FIG. 1 is a curve indicating the effect of an electrolyte composition changes in preparing an etched surface in accordance with this invention;

FIG. 2 is a photomicrograph of an etched tantalum foil surface created in accordance with this invention at 200 times its normal dimension; and

FIG. 3 is a photomicrograph of an etched tantalum foil surface created in accordance with a prior etching process at 200 times its normal dimension.

As an aid to understanding this invention it may be summarily explained as involving etched, inert valve metal surfaces as indicated in FIG. 2 of the drawings, these surfaces having high effective areas as opposed to initial surface areas and having a grooved type of comparatively uniform surface configuration. Such etched foils are, in accordance with this invention, created by electrochemically etching these surfaces using an electrolyte composition containing at least one additive which is considered to facilitate the removal of metal so as to achieve a desired type of etched surface configuration as indicated in FIG. 2 of the drawings.

Although this invention primarily pertains to etched tantalum foil electrodes such as electrodes created from cold-rolled tantalum foil, it is not limited to this type of electrode structure. This invention within its broader scope encompasses inert valve metal electrodes of any desired shape or configuration formed out of valve metals tantalum, niobium, and titanium and various alloys of these metals which are grain oriented and which are capable of being used in the same manner as these metals themselves in electrolytic capacitors as electrodes. Thus, the present invention encompasses not only metallic grain oriented foil electrodes but other grain oriented electrode structures such as etched electrodes having a cup-shaped appearance, etched wire electrodes or etched slug electrodes. With electrodes of various shapes as indicated, considerable variations in electrode thicknesses will be encountered. As a general rule, it is preferred to utilize the present invention with cold-rolled metal foils such as tantalum foils having a thickness of from about one-half mill to about one mill.

Any such electrodes having micro-crystalline grain oriented structures are at least to a limited extent influenced by manufacturing procedures and methods. It is presently believed that many such electrodes, such as inert valve metal foils, contain comparatively minute amounts of surface impurities which tend to affect the ability of such electrodes to be satisfactorily etched to high etch ratios. The presence of these surface impurities is normally detected when efforts are made to form or oxidize these foils at comparatively high voltages. While the precise nature of such impurities is not known, it is believed that they may consist of various surface oxides and compounds such as tantalum carbide, gases such as hydrogen, oxygen or the like located within the crystalline structures of electrode surfaces, and that the concentrations of such impurities will vary depending upon variations in such crystalline structures. Further, the amounts of such impurities are presently considered to be dependent upon not only manufacturing methods, but upon conditions to which such surfaces have been subjected after their manufacture.

In preparing the electrodes of this invention, in order to remove insofar as is possible these surface impurities, an unetched foil of such an inert valve metal may be first subjected to an initial cleaning step if its surface is not already substantially free from surface impurities. This cleaning step is considered to remove from its surface some

of the valve metal itself, and more important than this, various surface impurities of the type indicated above. In carrying out this cleaning step a valve metal, such as tantalum foil is made the anode in an electrolytic cell containing an inert cathode and a non-aqueous electrolyte which includes either a solvent or a solvent mixture and a non-film forming solute or solute mixture. The specific details of such cleaning step are given in full in parent Patent No. 3,190,822, identified hereinabove, the entire disclosure of which is incorporated herein by this reference.

A uniformly clean electrode surface is needed to facilitate the subsequent etching so as to enable the production of the type of etched surface configuration indicated in FIG. 2 of the drawings.

The solutes used in the electrolyte employed for the cleaning step herein specified should be of non-film forming ionogen type of and, of course, they should be soluble in the solvent or solvent mixture employed. Suitable solutes are compounds furnishing halide ions in the solvents.

This cleaning step is in the general nature of a polishing step and, as indicated in the preceding, is primarily intended so as to remove surface metal containing impurities and not to accomplish any material etching of an electrode surface. Because of this the conditions under which it may be carried out are primarily of a type well-known in the electrolytic field. Thus, the temperature of this initial cleaning step may be varied in practice so as to encompass a range of temperatures from about 20° C. to about the boiling point of an electrolyte used. In general the higher the temperature the more rapidly metal is removed from an electrode surface. Satisfactory results can be achieved at room temperature.

Similarly the current and voltage used during this cleaning step may be varied with comparatively wide limits. In general sufficient total charge should be used so as to remove substantially all surface impurities. The amount of such total charge will depend upon the amount of such impurities present upon an electrode surface being cleaned or polished.

The current form used during a cleaning step as herein specified may be varied over comparatively wide limits. It is preferred to etch with a combined A.C. and D.C. voltage where the R.M.S. value of the A.C. voltage component is approximately equal to the D.C. voltage impressed. However, it is possible to utilize during this cleaning or polishing step square wave form currents and to periodically reverse the polarity in the electrolytic cell employed.

The voltages used during a cleaning or polishing operation as herein described will vary depending upon the specific resistance of the electrolyte employed as well as the spacing of the anode and the cathode in any cell used. In general, the peak voltages should be held below a value at which scintillation will occur. Similarly the current densities used may be varied within comparatively wide limits. In general the greater the current density the greater the amount of metal removed and the greater the amount of heating within an electrolytic cell. Satisfactory results have been achieved using current densities of from about 20 to about 60 milliamperes per square inch of electrode surface and voltages consisting of an A.C. half wave superimposed upon a D.C. voltage of equal magnitude to the magnitude of the R.M.S. value of the A.C. wave so that either the D.C. voltage or the R.M.S. value of the A.C. voltage used is from about 2.5 to about 125 volts.

Following the cleaning step indicated in the preceding discussion an electrode in accordance with this invention is electrochemically etched as the anode in a cell containing an inert cathode and an electrolyte composition separating these two electrodes. The preceding cleaning step may, of course, be omitted when foils capable of being directly etched are to be processed. As pointed out in the preceding such foils are considered to be substantially free from surface impurities.

The electrolyte composition used during this etching step is considered to be extremely important in obtaining

satisfactory etch ratios and in obtaining the structure of this invention. Basically such an electrolyte is the same as the electrolyte as used during the cleaning or polishing step previously described except for the addition of an additive which is capable of facilitating the removal of an inert valve metal from the surface of such a metal during the electro-etching step. Because of this it is possible to carry out the invention by adding to an electrolyte as previously described desired quantities of one or more additive compounds and to carry on the etching in the same cell used for cleaning. It is also possible to carry out the process of this invention by physically transferring electrodes from one electrolytic cell to another so that the cleaning and etching steps are carried out in separate cells instead of in the same cell.

Preferred additives used with the present invention are sulfoxide complexing agents which are soluble in anhydrous methanol or similar solvents, which additions fall within the following general formula



in which the radicals R_1 and R_2 are of an inert character. Particularly suitable compounds falling within this general formula are dimethyl sulfoxide, diethyl sulfoxide, methylethyl sulfoxide and diphenyl sulfoxide. Other complexing agents such as pyrridine and similar heterocyclic organic compounds containing nitrogen in the ring structure or substituted derivatives of such compounds in which the ring substituted substituents are of an inert character or such as carbon disulfide are considered to be capable of being used in achieving at least some advantages in etching inert valve metals during this step of the present invention. A mixture of complexing agents as well as a single such agent can be employed in the etching electrolyte. Solubility of such an agent or agents in the solvent mixture employed is, of course, required.

The electrolyte used during this etching step may contain comparatively small or trace quantities of water. It is presently believed that up to about 1,000 parts per million of water on the basis of the total solvent or solvent mixture present does not detrimentally affect the character of the etch obtained in accordance with this invention. Greater proportions of the water than this are preferably avoided in practicing this invention inasmuch as such greater proportions of this contaminent tend to cause perforation of an electrode surface during electro-etching, and as a general rule this is to be avoided in achieving the preferred type of etched surface as indicated in FIG. 2 of the drawings. Similarly the presence of ketones such as acetone should be avoided in an electrolyte used during this electro-etching step for substantially the same reasons. Also, various contaminants of this type tend to decrease to a substantial extent the etch ratios which can be achieved in accordance with this invention for various reasons which are at the present time not completely understood or known. Many salt-type contaminants such as anhydrous magnesium perchlorate also detrimentally affect the etching process achieved in accordance with this invention.

The amount of an additive as herein specified which may be added to an electrolyte may be varied within comparatively wide limits. In FIG. 1 of the drawings there is shown a curve indicating variation in etch ratios achieved with cold-rolled tantalum foils processes as described in the examples indicated later in this specification. In this curve the affects of the addition of dimethyl sulfoxide to a specific anhydrous methanol electrolyte are shown. The amounts of dimethyl sulfoxide added to this electrolyte are shown on the basis of parts by weight. From this curve it will be seen that comparatively high etch ratios can be achieved by the addition of from about 0.5% by weight of this additive to about 70% by weight of this additive. The effectiveness of the use of an additive of the type indicated over this entire range is considered to be extremely significant.

This effectiveness is not completely understood at the present time. It is considered that an additive, such as dimethyl sulfoxide, used during the etching step of the present invention does not directly affect the precise etching reactions occurring directly upon an electrode surface, but that it indirectly affects such reactions by tending to facilitate the removal of inert valve metal from such a surface. It is believed that in all probability an additive as herein described operates in the process of this invention so as to form a solvated complex with a valve metal such as tantalum which is attacked during the etching operation. It is also believed that such a complex places such a valve metal into a form where it is removed from the innerfacial areas where electrode reactions take place, thus facilitating the etching operation. It is also believed that water interferes with the etching reaction by hydrolyzing the complex ion and forming an insoluble hydrated oxide which may coat the surface and interfere with the flow of current to specific sites on the metal surface. It is presently believed that comparatively small trace-quantities of such contaminants effectively inhibit or prevent this type of action. This is shown in the point A in FIG. 1 indicating an electrolyte having a composition as shown by the curve containing 4.2 parts by weight of water on the basis of the weight of the solvent employed. This water causes slightly in excess of a 50% drop of etch ratio which could be achieved with this invention.

In general the temperature and electrical conditions under which an electro-etching step as herein specified was carried out are substantially the same as the conditions used in carrying out an electro-cleaning step as previously specified. For this reason it is not considered necessary to repeat the preceding discussion as to temperature, voltages, currents and the like. The amount of total charge used during the etching will, of course, effect the amount of etching achieved and, hence, will vary the etch ratio obtained in a final electrode. As a general rule it is desired to carry out the electro-etching so as to achieve as high an etch ratio as possible and to use no more charge than is necessary in order to achieve such an etch ratio since etching beyond a maximum etch ratio only serves to remove metal and, hence, serves to weaken the mechanical structure of an electrode. The amount of total charge which would be used in etching will vary somewhat depending upon the final results achieved with this invention. In general, however, it can be stated that satisfactory etch ratios can be achieved by passing from about 160 to about 200 coulombs of charge per square inch of electrode surface etched.

It will, of course, be realized that the final etch ratio achieved on any electrode surface is normally determined by means of capacitance measurements taken after such a surface is anodized in accordance with conventional practice. Depending upon the conditions of such anodization the etch ratio which is measured for any electrode will vary over comparatively wide limits. Thus, for example, cold rolled tantalum foils which have been cleaned and etched in an identical manner in accordance with this invention have been determined to have an etch ratio of about 14 when formed in accordance with conventional practice at 25 volts and of about 5 when formed at 180 volts under identical conditions except as to voltage.

From an examination of FIG. 2 of the drawings showing an etched surface created in accordance with this invention it will be realized that these etched surfaces as herein described are of a comparatively uniformly etched character, and that when viewed under a microscope they have the essential appearance of a series of ridges and valleys, these ridges and valleys being substantially regularly located parallel to one another and all having an unven surface configuration. This regularity and the distance between successive ridges is determined by the fineness of the metallographic grain and the direction of the valleys and ridges is determined by the direction of rolling of the metal and thus the grain orientation. This results from the fact that the rolling operation breaks down crystals into smaller ones and the fragments are laid out along lines parallel to the rolling direction. Plastic deformation also takes place to elongate individual grain structures. The fineness of the grain is of particular importance therefore to the ratios of surface developed on etching and metal having the maximum degree of cold working by rolling, extruding or drawing is much to be preferred.

This type of etched surface is considered to be different in kind from etched surfaces of the general variety indicated in FIG. 3 of the drawings created in accordance with known techniques. Etched surfaces made by prior techniques on tantalum and other inert valve metals are of essentially a pock-marked configuration and they appear to be essentially smooth except where they are intersected by what may be termed "holes" extending into the metal surface. The smooth areas in prior art electrodes as indicated in FIG. 3 are considered to be areas where no significant increase in effective surface area has been achieved by the etching process used in creating them. The smooth areas seen on the prior art electrode surface represent areas which have been essentially left untouched by the electrochemical reaction and it is believed that these may be caused by very thin films of compounds of tantalum which are resistant to etching and that with prior processes the etching action achieved primarily follows boundry lines between crystalline regions in the foil being treated. The reduced etch ratios obtained in the prior art thus appear to be due to the fact that not all the metal surface comes into play. The amount of tantalum dissolved in forming the electrode surfaces shown in FIGS. 2 and 3 was exactly the same. Another advantage of the present invention is that it can be a very thin foil, as low as 0.2 mil, without perforation. Thus, strength of a foil in accordance with this invention is greatly superior to a perforated prior foil.

As an aid to understanding this invention the following specific examples of carrying out processes as herein described in creating etched surfaces of the type indicated in FIG. 2 of the drawings are given. These examples are given by way of illustration only and are not considered as limiting this invention. For convenience of presentation these examples are set forth in tabular form. All of the examples pertain to the treatment of commercially available one-half inch wide cold-rolled tantalum foil. In all of these examples identical electrochemical cells are employed.

In all examples the etch ratios were determined after forming (oxidizing) the etched electrodes indicated to 25 volts at an electrolyte temperature of about 90° C. using 20 milliamp. current. The same current was used in all of the forming operations regardless of electrode size or the degree to which an electrode had been etched. In forming the electrodes in Example I the electrolyte employed contained: 60 parts by weight ethylene glycol; 40 parts by weight water; and 10 parts by weight oxalic acid. In Example II the electrolyte contained 1 part by weight ammonium phosphate and 1000 parts by weight water.

ELECTROCLEAN

Example No.	I	II
Anhydrous methanol, solvent, parts by weight		1.000
Ammonium bromide, solute, parts by weight		.050
Water, parts by weight		
Voltage, D.C.		4.0 to 3.0
Voltage, A.C.-R.M.S. value impressed on D.C. voltage		4.0 to 3.0
Current density, milliamps per sq. inch surface		40
Time, minutes		20
Total charge, coulombs per sq. inch foil		10.0
Temperature, °C. (initial)		20

ELECTROETCH

Anhydrous methanol, solvent, parts by weight	1.000	1.00
Ammonium bromide, solute, parts by weight	0.045	.041
Dimethyl sulfoxide, additive, parts by weight	0.125	.214
Water, parts by weight	.0005	.0005
Voltage, D.C.	3.1	3.0
Voltage, A.C.-R.M.S. value impressed on D.C. voltage	3.1	3.0
Current density, milliamps per sq. inch surface	40	40
Time, minutes	20	20
Total charge, coulombs per sq. inch foil	100	100
Temperature, °C. (initial)	20	20
Etch ratio	9.09	8.8

I claim:

1. An etched surface of an inert valve metal selected from the group consisting of tantalum, niobium and titanium, said surface being substantially free from surface impurities and having a surface appearance resembling a series of substantially parallel and regularly located ridges and valleys, said ridges and valleys having an uneven etched surface configuration.

2. A flat, cold-rolled tantalum foil electrode, said electrode having an etched surface which is substantially free from surface impurities and which has a microscopic appearance resembling a series of parallel substantially regularly located ridges and valleys, said ridges and valleys having an uneven surface configuration and being substantially uniformly etched.

3. A wrought capacitor electrode of an inert valve metal selected from the group consisting of tantalum, niobium and titanium, said wrought electrode being grain oriented in accordance with the physical working resulting in the wrought form thereof, said wrought electrode having a surface, said surface being substantially free of surface impurities and being etched, said etched surface having the microscopic appearance resembling a series of substantially parallel and substantially regularly spaced ridges and valleys, said ridges and valleys being organized with respect to the grain orientation of said wrought electrode, said ridges and valleys providing an uneven surface configuration and being substantially uniformly etched.

4. A wrought tantalum capacitor electrode, said wrought electrode being grain oriented in accordance with the physical working resulting in the wrought form thereof, said wrought electrode having a surface, said surface being substantially free of surface impurities and being etched, said etched surface having the microscopic appearance resembling a series of substantially parallel and substantially regularly spaced ridges and valleys, said ridges and valleys being organized with respect to the grain orientation of said wrought electrode, said ridges and valleys providing an uneven surface configuration and being substantially uniformly etched.

5. An etched tantalum foil electrode having a surface configuration as shown in FIG. 2 of the drawing.

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DAVID L. RECK, *Primary Examiner.*

R. O. DEAN, *Assistant Examiner.*