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**3,203,793**  
**POROUS COLUMBIUM AND TANTALUM**  
**MATERIALS**

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This is a continuation-in-part of application Serial No. 137,958 filed September 14, 1961, now abandoned.

This invention relates to novel metal products which can be anodized to give improved electrodes, to processes for producing such metal products, and to improved electrolytic capacitors having electrodes made from the metal products.

A method has now been found for producing columbium and tantalum base components which make possible electrolytic capacitors of higher capacitance and lower leakage currents than those previously obtainable. This method comprises heating a shaped metal body consisting essentially of at least one metal from the group of columbium and tantalum and at least one alloying metal from the group of titanium and vanadium, the heating being carried out under reduced pressure, that is, below atmospheric pressure, and at a temperature of at least 1600° C., and below the melting point of the shaped metal body. Under these conditions, titanium and vanadium are volatile, having appreciable vapor pressures, and boil out or evaporate from the metal body.

As a result of this evaporation, the metal body becomes porous and develops an increased surface area which makes the metal more suitable for use in electrolytic capacitors in that more effective area of electrode per unit weight metal is formed. The porous surface is of such a character as to permit the formation or deposition thereon of high dielectric-strength oxide coatings during subsequent anodization.

The products of the heating process of this invention are considered to be novel, and they are comprised of a shaped metal body having a porous surface consisting essentially of a metal from the group consisting of columbium, tantalum, and combinations thereof. They have a roughness factor which is at least 3 and which remains substantially unchanged upon anodization to 200 volts.

What is important in the metal products of this invention is the composition of the surface exposed to anodization, rather than the overall composition of the metal bodies. This surface is relatively pure columbium or tantalum or a combination of these metals. In regions of the metal bodies away from the surface it is quite possible to have residual titanium or vanadium or other metals, provided such regions are not reached and exposed by the anodizing treatment.

The surface purity can be demonstrated by the following techniques:

The porous metal body is anodized to 200 volts at 25° C. by electrolyzing it in a 0.01% by weight solution of orthophosphoric acid in water. This forms on the surface a thin layer of oxides of the metals in such surface.

This anodic film is isolated by leaching away the metal immediately underlying it, using as the leaching reagent a 10% by volume solution of bromine in methanol. The isolated film is then analyzed by emission spectrographic methods.

By the foregoing test it is found that the anodic oxide films on metal bodies prepared by processes of this invention have contamination levels of not over about 10% by weight. Constituents other than columbium, tantalum and oxygen are considered to be contaminants in the oxide film. To gain the maximum improvement in the novel metal bodies the concentration of contaminants in the anodic oxide film should be below about 1% by weight.

The manner in which enhancement of the electrical properties of anodes prepared from novel metal products of this invention is effected may be illustrated by consideration of the novel processes as applied to Nb-Ti binary alloys. The alloys which are to be heat-treated are first prepared by melting and remelting together weighed portions of the pure metals to obtain a homogeneous alloy button which is then rolled to a foil of uniform thickness. Electrodes cut from this foil are heated under vacuum so that the lower melting metal, titanium in this case, volatilizes. The vapor pressure of titanium is great enough, even at temperatures considerably below the melting point of the Nb-Ti alloy, to develop cavities near the foil surface. The vapor pressure of titanium in these cavities is relieved through creation of channels opening to the outer periphery of the specimen, and pores are formed on the surface extending more or less deeply into the body of the foil.

One possible explanation of the operation of the process is that the alloys become plastic at the temperatures involved. The specimen becomes increasingly rigid as its composition changes due to the evolution of the more volatile metal. This increased rigidity is due to the increase in melting point of the alloy as it becomes richer in the high melting point refractory metal and loses more of the lower melting, more volatile metal. Because of this change in melting point with changing composition, a means exists by which vapor pores are created and frozen in place before coalescence or collapse can occur. While this explanation appears to fit the facts, it is not to be considered as limiting, the scope of the invention being as defined in the appended claims.

Although this discussion of the process by which the porous anode material is formed has been illustrated by reference to a Nb-Ti binary alloy, the same explanation is equally applicable to the formation of porous materials wherein vanadium or a combination of vanadium and titanium is evaporated from columbium or tantalum or from an alloy comprising a combination of these two refractory metals.

The shaped metal electrodes are anodized for use in electrolytic capacitors by well-known methods. These methods of anodizing are described in the literature. See, for example, "Fixed and Variable Capacitors," by Dummer and Nordenberg (McGraw-Hill, New York, 1960) Chap. 9.

The alloys can be prepared by blending columbium and/or tantalum with titanium and/or vanadium in the

proportion desired and melting in an inert atmosphere. A useful property of these alloys is that buttons or ingots prepared in this way are homogeneous solid solutions and may be formed readily by conventional metal working operations into shapes appropriate for capacitor electrodes, such shapes including foils, sheets, wires, woven wire fabrics, or in short solid objects of any useful geometry in which highly developed surfaces may be achieved by the method described above. For example, buttons of Nb-Ti or Ta-Ti prepared by direct melting may be rolled to foil directly at room temperature and without intermediate heat-treatment or annealing between successive rolling operations. The shapes so produced are usually cleaned with conventional reagents before the heat-treating step.

In a process of this invention, the heating period has ranged from 15 minutes to 6 hours at temperatures within the range of 1600° C. to 2100° C. in vacuum of about 10<sup>-4</sup> mm. Hg. The time and temperature of the heating vary with the alloy composition, the initial thickness of the alloy body, and the degree of porosity which is desired in the alloy surface.

After heating, the porous metal body can be anodized to form a thin dielectric film of oxide on its surface. The anodization is carried out at constant current density until a desired voltage is reached as in the usual practice. In the examples which follow, the dielectric oxide coating was formed to 200 v. at a temperature of 25° C., by electrolyzing in 0.01% H<sub>3</sub>PO<sub>4</sub> (wt. percent).

It has been shown that formation can be effected to very high voltages without damage to the anodic layer. For example, a Ta-Ti derivative was formed in 0.01% propionic acid to the scintillation voltage of the electrolyte (550 volts) without evidence of anodic film degradation, which would be shown by increased slope in the logarithmic plot of D.C. leakage vs. formation voltage. Thus, full utilization of the high voltage characteristics of this anode material is now only electrolyte-limited.

After formation, D.C. leakage through the oxide film remains at a low level at room temperature. Increase in D.C. leakage from -55° to +85° C. is approximately exponential. These facts demonstrate good blocking behavior of the anodic layer in this temperature range.

After the damage which usually occurs during application of MnO<sub>2</sub> counterelectrode in the case of solid electrolyte devices, alloy derivatives can be rehealed readily. Voltages up to 200 volts in the first reheal, and 120 volts in the third reheal, have been obtained on Ta-Ti derived anodes.

In the case of wet electrolyte devices, the encapsulated unit can be rehealed to 70% of formation voltage with preservation of very low D.C. leakage.

No significant deterioration of the anodic layer formed on a Ta-Ti derivative was observed after 6 months immersion in 35% H<sub>2</sub>SO<sub>4</sub> at room temperature. Upon application of voltage, the initial low D.C. leakage was rapidly reattained.

Excellent anodic characteristics have been observed on anodes prepared from a variety of initial compositions and under varying vacuum heating conditions, indicating the reproducibility of film quality.

Extensive investigation has resulted in a large body of information which illustrates how capacitance of an alloy-derived anode varies with respect to (1) initial alloy composition, (2) specimen geometry, and (3) temperature-time programming during vacuum heating. As a result of these investigations, it is possible to choose optimum conditions for maximum capacitance development in the case of alloy sheets. Capacitance gain or ratios of capacitance to that of a plain sheet formed under identical conditions, ranging up to 38 on thick (initially 0.025 in., finally 0.015 in.) Ta-Ti derived sheet have been measured.

Capacitance gain in the alloy-derived anodes is, to a first approximation, independent of formation voltage up to about 500 volts. Capacitor grade Ta foil can be etched electrochemically to show gains up to 4-5 at very low formation voltages (ca. 15 volts), but the gain disappears at formation voltages above 150 volts.

When the pertinent variables are properly controlled, capacitance per area values can be reproduced readily in the alloy-derived anodes, indicating that final devices can be made with a high degree of precision, probably of the order of ±5%. Capacitors made from electrochemically etched foil show capacitances reproducible within +20 to -50%.

High quality of the anodic oxide film leads to low inherent dissipation factors. Also, resistive losses are low because the relatively large pore size in the anodes makes possible low resistance paths in the counterelectrode.

It appears that the high quality of the anodic layer results from a high degree of perfection in the anode surface. High fluidity of the specimens during vacuum heating and Ti evolution probably results in a highly homogeneous distribution of impurities in the lattice of the residual metal. Further, this condition appears to allow a closer approach to equilibrium insofar as the recrystallization tendencies are concerned, allowing the anode surface, although polycrystalline, to attain a nature approaching that of a nearly perfect single crystal.

In the work that was carried out on this invention, electrical properties of the anodized specimens were tested in an electrolyte consisting of 10% H<sub>3</sub>PO<sub>4</sub>. Leakage current was measured at 25° C. after 5 minutes of electrification at 80% of forming potential. Capacitance and dissipation factors were measured with a 120 c.p.s. 1 volt A.C. signal under a 10 volt D.C. bias at 25° C.

For a clearer understanding of the invention, the following specific examples are given. These examples are intended to be merely illustrative of the invention and not in limitation thereof. Unless otherwise specified, all parts are by weight.

#### EXAMPLES 1 THROUGH 13

Columbium-titanium alloys consisting of, by weight, 90% columbium and 10% titanium; 70% columbium and 30% titanium; 60% columbium and 40% titanium; 50% columbium and 50% titanium; 40% columbium and 60% titanium; and 30% columbium and 70% titanium were prepared by melting and remelting together proportionate amounts of these metals. The resulting homogeneous alloy buttons were rolled to 0.007" foil by repetitive rolling operations but without intermediate annealing and from these foils test specimens ½" x 1" were cut. These pieces were precleaned by washing in trichloroethylene, acetone, and distilled water, and air dried. The specimens were heated in vacuum at temperatures of 1700° C., 1800° C., 1900° C., 2000° C., and 2100° C., for one hour. Following these heat treatments, the specimens were anodized, using an electrolyte comprising 0.01% H<sub>3</sub>PO<sub>4</sub> in water. The current density used to form the oxide film was 200 milliamps/in.<sup>2</sup>, and the oxide film was formed to 200 v.

The specimens were removed from the electrolyte, washed in distilled water at 90° C., for one hour, and air dried. They were then tested for electrical properties, and these are given in Table I.

For comparison of electrical properties of the heat-treated specimens with those of the control samples, specimens cut from rolled foil were treated and tested in exactly the same way as the alloy samples described above except that the step of heat treating in vacuum was omitted. The capacitance of these unheated samples and the leakage currents are also given in Table I.

Table I.—Electrical properties of anodized specimens derived from Nb-Base alloys

[ELECTRICAL PROPERTIES AFTER ANODIZATION]

Example	Alloy comp. before heating (wt. percent)		Heat treatment prior to anodization (1 hr.-vacuum), ° C.	Percent wt. loss on heating	Capacitance $\mu\text{fd./in.}^2$	Leakage current, $\mu\text{a./}\mu\text{fd. V.}$	Dissipation factor, percent
	Nb	Ti					
Control.....	100		2,100	-----	0.98	0.0060	1.00
Control.....	70	30	None	-----	0.52	0.144	-----
Control.....	50	50	None	-----	0.57	5.17	-----
1.....	90	10	2,000	2.1	1.02	0.0058	0.80
2.....	70	30	1,700	(*)	1.55	0.0091	-----
3.....	70	30	1,800	(*)	1.41	0.0053	1.58
4.....	70	30	1,900	10.8	4.81	0.0042	3.00
5.....	70	30	2,000	17.5	6.83	0.0041	1.10
6.....	50	50	1,900	42.4	14.21	0.0030	3.70
7.....	50	50	2,000	48.5	15.4	0.0040	2.20
8.....	40	60	1,700	(*)	2.08	0.0667	8.00
9.....	40	60	1,800	(*)	8.43	0.0119	3.36
10.....	40	60	1,900	(*)	0.92	0.0118	3.20
11.....	30	70	1,700	(*)	1.62	0.0838	2.96
12.....	30	70	1,800	(*)	5.87	0.0167	1.96
13.....	30	70	1,900	(*)	7.64	0.0198	2.44

\*Not determined.

#### EXAMPLE 14

A foil was prepared by melting together 40 parts by weight of titanium metal powder and 60 parts by weight of columbium metal powder, and rolling the resulting ingot to a thickness of 0.007" as in Examples 1-13. Photomicrographs of the foil at 500 $\times$  showed a smooth surface. A portion of this foil was then treated in vacuum at 1700° C. for a period of one hour, and photomicrographs were made which showed substantial porosity in the surface. Three other foil specimens were also cut from the same rolled piece, and one heated in vacuum for 1 hour at 1800° C., one for 1 hour at 1900° C., and one for 1 hour at 2100° C. An increase in surface area, as indicated by the porosity of the surface, in photomicrographs at 500 $\times$  showed that the surface area increased with increasing temperature of heat treatment. The foil heated at 2100° C. showed the greatest surface area. X-ray fluorescence intensity measurements on the surface of the foil after heating for one hour in vacuum at 2100° C. established that there was less than 0.1% titanium on the surface. The X-rays in this test penetrate the metal surface to a depth of 0.003".

In a similar manner, an alloy foil of 50% by weight columbium and 50% by weight titanium was prepared by melting and rolling a foil of 0.007" thickness from the ingot. Portions of this foil were heated under vacuum for one hour at 1700° C., 1800° C., 1900° C., and 2000° C. Portions of these heated specimens were examined under the microscope and photomicrographs were made. These showed that surface-roughening and porosity resulted in these specimens due to the evaporation of the lower melting metal, and this roughening and porosity increased with heating at higher temperatures.

#### EXAMPLE 15

Separate specimens of an alloy consisting essentially of 75% tantalum and 25% titanium were heated at 1700° C., 1900° C., and 2100° C. for one hour in a vacuum and in each instance the alloy was anodized and then tested in the same manner as previously described. Capacitor components were also prepared in the same manner from alloys consisting essentially of 75% columbium and 25% vanadium; and from 75% tantalum and 25% vanadium. The results of heating these alloys under vacuum, anodizing the resulting porous foil, and testing in the same manner as previously described, are summarized in Table II.

Table II

Nb	Alloy composition before heat treatment			Heat treatment prior to anodization (1 hr.-vacuum), ° C.	Capacitance, $\mu\text{fd./in.}^2$	Leakage current, $\mu\text{a./}\mu\text{fd.}$
	Ta	Ti	V			
--	75	25	--	1,700	1.30	0.0202
--	75	25	--	1,900	2.16	0.0306
--	75	25	--	2,100	3.32	0.0082
--	75	25	--	(*)	0.475	1.97
75	--	--	25	2,100	3.65	0.0104
--	75	--	25	2,100	3.50	0.0075

\*No heat treatment before anodization.

From the above, it is seen that useful electrolytic capacitor components can be prepared from either tantalum or niobium alloyed with either vanadium or titanium. It is also contemplated to use combinations of these materials.

Since one purpose of this invention is to improve the capacitance capability of the porous metal body, the most direct way to characterize the products of this invention is in terms of the superior capacitance of capacitors made therefrom. From the data presented in Table I, it will be seen that among the prior art control materials tested, unalloyed columbium showed the highest capacitance per unit area; that is to say, apparent, projected or geometric area. It can also be seen from Table I that the present invention produces materials having at least 4% more capacitance per unit area than that from unalloyed columbium (see Example 1). Moreover, in the case of Example 7, there is over a 15-fold increase in capacitance as compared with unalloyed columbium.

The increased capacitance obtainable according to this invention is a result of the porous nature of the surface of the metal. This porosity is caused by the escape of the metal body during heating, leaving an uneven surface of increased surface area. This increased surface area can be measured by the conventional Brunauer-Emmett-Teller Gas Adsorption Method, using krypton as the adsorbed gas. The ratio of the B.E.T. measured area to the geometric surface area, as determined by the length and width dimensions of the metal piece, gives a numerical value which is referred to as the "roughness factor." Products prepared by this invention have roughness factors of from 3 to 15 or higher, and these factors do not change substantially—that is, by more than about 10%, when the products are anodized to 200 volts. In con-

trast, conventional non-etched metal foils have a roughness factor which does not exceed 1.6.

Among the products treated according to this invention were 3 foils having a thickness of 2, 4, and 7 mils, respectively, made from a 50% Nb-50% Ti alloy. The two-mil foil was held under vacuum at 2000° C. for 15 minutes; the 4-mil foil was held under vacuum at 1900° C. for 30 minutes; and the 7-mil foil was held under vacuum at 2000° C. for 1 hour. The roughness factors were found to be 3.74, 6.15 and 12.2, respectively, by B.E.T. adsorption measurements. The capacitance values after anodization were found to be 4.71, 10.43, and 15.4 times the value of that of a pure columbium foil anodized under the same conditions.

It will be seen from the results given in Table I above that the anodes which have been prepared according to the process of this invention exhibit exceptionally low dissipation factors considering the large surface enhancement factors. This improvement is attributed to the nature or character of the pores developed in the surface of the electrode metal by the methods of this invention. The surfaces contain pores of an open structure with smooth walls and rounded closed ends, so that permeation of electrolyte when anodizing the electrode is facilitated with formation of anodic oxide films on all surfaces. Similarly, in finished capacitor devices, the counterelectrode, whether liquid, gel, or semiconducting solid, has ready access to the whole highly developed surface of the electrodes of this invention. When enhancement of the surfaces of capacitor electrode materials is attempted by etching with acids, a procedure by which the metals are attacked preferentially at metal grain boundaries, removal of metal from these boundaries increases the effective surface but not to the extent described in this invention; furthermore, the pores so produced are of a V-shaped or crevasse-like character which do not so readily permit full penetration by forming electrolytes or counterelectrolytes, and which as a consequence of their shape, lead to higher dissipation factors on the finished device. A further disadvantage of enhanced-surface metal bodies produced by etching is that the crevasse-like pores are soon filled up with oxide in the course of anodification and therefore the full benefit of surface area enhancement achieved by this means is lost upon forming to higher voltages. By contrast, the effective area of surface-enhanced anodes made according to this invention is independent of forming voltage up to at least 200 volts.

The novel alloys can be used as electrodes in whatever shape desired. Electrodes are commonly prepared from foil, but in certain instances it may be convenient to use the alloy in the form of wire, or in any geometric form appropriate to the design of the capacitor.

In the anodization of the specimens described above, the use of phosphoric acid has been found to be a satisfactory forming and testing electrolyte. However, the invention is not limited to the use of this or any other specific forming or testing electrolyte as the improved properties in the capacitor component parts are not in general dependent upon the use of any specific electrolyte.

I claim:

1. A porous metal product having a roughness factor which is at least 3 and remains substantially unchanged upon anodization of the product to 200 v., said product comprising a porous metal body having pores therein originating in cavities near the body surface, the cavities opening through channels to the outer periphery of the body, the surface of said body, including the surface of the pores therein, consisting essentially of a metal from the group consisting of columbium, tantalum, and combination thereof, the purity of said surface metal being such that when the body is anodized to 200 volts at 25° C. by electrolyzing it in a .01% by weight solution of orthophosphoric acid in water, the concentration of contaminants in the anodic oxide film so formed on its surface is below about 1% by weight, constituents other than columbium, tantalum and oxygen being considered contaminants, and there being in regions of said porous body away from its surface, in addition to the metal of the group consisting of columbium, tantalum and combinations thereof, a metal of the group consisting of titanium, vanadium, and combinations thereof.
2. A porous metal product of claim 1 wherein the metal is columbium.
3. A porous metal product of claim 1 wherein the metal is tantalum.
4. An electrolytic capacitor comprising as an anode therein an anodized porous metal product of claim 1.

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DAVID L. RECK, *Primary Examiner.*