United States Patent [19]
Ronneau et al.

[11] **3,867,129**
[45] **Feb. 18, 1975**

[54] ANODICALLY OXIDIZABLE METAL POWDER

[75] Inventors: **Gerard S. Ronneau**, Edegen; **Pierre D. Debacker**, Hoboken; **Hugo L. Carpentier**, Aartselaar, all of Belgium

[73] Assignee: **Metallurgie Hoboken-Overpelt**

[22] Filed: **Feb. 5, 1974**

[21] Appl. No.: **439,805**

[52] **U.S. Cl.**......... **75/0.5 BB**, 29/192 R, 29/192 CP, 75/174
[51] **Int. Cl.**........................... **B22f 9/00**, C22c 27/00
[58] **Field of Search**............ 29/192 CP, 192 R, 182; 75/0.5 BB, 0.5 BA, 174

[56] **References Cited**

UNITED STATES PATENTS

3,203,793	8/1965	Hand	75/174
3,285,716	11/1966	Contant	75/174
3,415,639	12/1968	Daendliker et al.	75/0.5 BB

Primary Examiner—W. Stallard
Attorney, Agent, or Firm—Fred Philpitt

[57] ABSTRACT

An anodically oxidizable metal powder for use in electrolytic capacitor applications, the individual metal particles containing in depth and/or surface evenly or unevenly distributed amounts of the metals molybdenum and/or vanadium and/or tungsten and/or hafnium.

6 Claims, No Drawings

ANODICALLY OXIDIZABLE METAL POWDER

The present invention relates to improvements in powders used in the manufacture of electrolytic capacitors.

It is well known that electrolytic capacitors have to meet a large number of conditions which it is difficult to obtain simultaneously as they are often contradictory. In the present state of the technique and taking into account the intrinsic characteristics of the powders used in building up a capacitor, such as tantalum or niobium powders, there is some difficulty in achieving an acceptable compromise amongst the various electrical characteristics demanded of a capacitor.

The new powders, object of the present invention, provide the means of solving the above problem as will appear from the examples of comparable results set out in Table I hereafter.

In accordance with the present invention there is provided a metal in powder form, whose particles are made up of an anodically oxidizable metal, also recognized as valve metal or metal converting alternating current to direct current, such as tantalum or niobium powder, containing molybdenum and/or vanadium and/or tungsten and/or hafnium in contents comprised between 0.06 and 2 per cent on an additive metal to tantalum or niobium metal basis, these additive metal contents referring to each additive metal separately or to the additive metals as a whole.

The particles of another powder according to the invention are made up of a nucleus of anodically oxidizable metal covered with a surface layer of the same metal, such layer containing molybdenum and/or vanadium and/or tungsten and/or hafnium in contents comprised between 0.01 and 2 per cent on an additive metal to tantalum or niobium metal basis, these additive metal contents referring severally to each additive metal separately or to the additive metals as a whole. The thickness of said surface layer will preferentially be less than 3,000 Angstrom.

Still another powder according to the invention is one whose particles are made up a nucleus of anodically oxidizable metal covered with either a continuous or a noncontinuous surface layer, or one or more areas on the surface, made up of molybdenum and/or vanadium and/or tungsten and/of hafnium. The thickness of said surface layer will preferentially be less than 3,000 Angstrom.

It has been found that powders according to the invention improve the characteristics of the dielectric (electrolytic oxide) built up on the surface of the particles of which these powders are made up. Such improved characteristics give better performance to the capacitor manufactured from these powders. In effect, it has been found on such capacitors manufactured from powders according to the invention a sizeable decrease of the capacitance variance as a function of operating temperature; in addition, such capacitors withstand reverse voltages higher than those that can be withstood by capacitors manufactured from a powder that has not been treated according to the present invention and the performances under life test are better.

The powders according to the present invention can be manufactured by a number of well known methods such as: co-fusion and embrittlement, sodiothermic reduction, fused electrolysis, hydrogen reduction on a fluidized bed.

a. One suitable powder which can be processed in accordance with the present invention is a tantalum powder obtained by electron-beam fusion and hydrogen embrittlement. Such high-purity powder is thoroughly blended with molybdenum powder in proportion of 100 to .2 by weight. The powder blend is compacted in an isostatic press by a well-known technique and the resulting bars are melted in an electron beam furnace. The ingot is hydrided to a hydrogen content of about 0.4 per cent by weight, then it is crushed and pulverized and the powder obtained is degassed and submitted to chemical assay. The desired molybdenum content is traced back in the powder with more or less 10 per cent accuracy.

b. Another type of powder which can be prepared in accordance with the present invention is made by charging a quantity of potassium double fluoride into a sodiothermic reduction vessel. The reduction occurs at a temperature of about 800°C in a fused salt solution containing sodium chloride: for instance 300 kg of potassium tantalum double fluoride in 10 kg sodium chloride. A stoichiometric quantity of sodium in liquid form is slowly added to the fuses salt mass; a dendritic tantalum powder is rapidly formed. When the reaction signs (exothermicity) tend to disappear, indicating that the chemical reaction has been completed, a quantity of 260 g of vanadium trichloride is charged into the sodiothermic reduction vessel, then 120 g of sodium are added. After crushing the sponge containing the tantalum, and washing the crushed sponge, a tantalum powder is obtained which contains about 600 parts per million of vanadium, this latter metal being located on the surface of the powder particles. c. Still another type of powder which can be prepared in accordance with the present invention is made by an operating process similar to the one described just above. The particles of this powder show a surface layer containing both the matrix metal, which is tantalum or niobium, and the doping element. To this end, the reaction, scheduled for reducing 300 kg of potassium tantalum double fluoride is stopped when 90 per cent. of the required quantity of sodium has been added; then a reducible compound, as in the process described above, is injected into the reaction vessel. Then the addition of sodium is resumed and the reduction together of the remaining 10 per cent. of the matrix metal and of the additive element occurs simultaneously on the surface of the powder particles obtained during the first phase of the reaction.

EXAMPLES.

Table I below records the results of measurements made on electrolytic capacitors manufactured from two powders of the invention; more explicitly, one of these powders was made according to example (a) above; it is referenced in table I by the letter (a); it contains on average 2,100 parts per million by weight of molybdenum (0.21 per cent). The other powder was made according to example (c); it is referenced in table I by the letter (c); it contains on average 1050 parts per million by weight of molybdenum (0.105 per cent.). For purposes of comparison, table I also includes the resultats of measurements made on capacitors manufactured from a powder such as can be found on the market, being powder P38 from Reframet-Hoboken. This powder represents the status of performance that can presently be achieved without the improvements brought by the powders of the present invention; it was manufactured according to the procedure of example (a); nevertheless, contrary to the invention, it does not contain any traceable amount, added naturally, accidentally or intentionally, of molybdenum or vanadium or tungsten or hafnium that can be determined by chemical analysis.

The electrolytic capacitors manufactured from these three powders are of type C 40 volts and 50 volts with solid electrolyte (manganese dioxide) and manufactured by a strictly identical process, so as to lend results an absolute value for purposes of comparison.

Under Section A of Table I, characteristics of capacitor anodes will be found such as they can be measured in a liquid electrolyte of phosphoric acid before insertion into the capacitor case and before impregnation with manganese nitrate, each of these steps being well known by the trade.

Section B of Table I lists the main characteristics of finished electrolytic capacitors, such as capacitance, leakage current and dissipation factor, but the significant parameters of variance of capacitance in relation to capacitance at 25°C for capacitances measured at –55°C, 85°C and 125°C.

Δ cap.(–55°C) is the ratio capacitance at –55°C - capacitance at 25°C/capacitance at 25°C

Δ cap.(85°C) is the ratio capacitance at 85°C - capacitance at 25°C/capacitance at 25°C

Δ cap. (125°C) is the ratio capacitance at 125°C - capacitance at 25°C/capacitance at 25°C

these ratios being expressed in percentage points in Table I. The significant advantage provided by the powders of the invention over another powder can clearly be seen; there is less capacitance variation.

From Section C it can be seen that the advantage of powders of the invention is also obvious with respect to leakage current of electrolytic capacitors manufactured from these powders as capacitors breaking down during life tests are on average fewer.

From Section D it will be noticed that capacitors made from the powders of the invention withstand higher reverse voltages (with negative polarization of tantalum) than capacitors made from other powders. This advantage is expressed in the leakage currents and the breakdown voltages.

TABLE I

Performance of type C capacitors

	Units	Untreated reference powder	Powder of the invention 1050 ppm Mo on the surface (c)	Powder of the invention 2100 ppm Mo in the matrix (a)	Untreated reference powder	Powder of the invention 1050 ppm Mo on the surface (c)	Powder of the invention 2100 ppm Mo in the matrix (a)
		A.- Anode characteristics (average of measurements on 500 anodes)					
Weight	g	1	1	1	1	1	1
Diameter	mm	4.47	4.49	4.48	4.47	4.49	4.48
Height	mm	7.36	7.32	7.33	7.36	7.32	7.33
Sintering temp.	°C	1850	1850	1850	1850	1850	1850
Sintering time	min.	30	30	30	30	30	30
Dissipation	%	14	14	14	14	14	14
Leakage	μAmp/g	0.57	0.80	0.71	0.57	0.80	0.71
Capacitance	μFV/g	3841	3858	3732	3841	3868	3732
		B.- Characteristics of type C capacitors 40 V and 50 V (average of 20 capacitors)					
		C/40 V			C/50 V		
Capacitance	μF	21.5	22.0	22.2	17.7	17.2	17.2
Leakage	μAmp/capacitor	0.087	0.141	0.084	0.166	1.08	0.25
Dissipation	%	1.67	0.88	0.86	1.38	0.86	0.88
Δ cap(–55°C)	%	–4.36	–2.32	–1.84	–3.9	–2.3	–1.74
Δ cap(+85°C)	%	+5.1	+2.72	+2.7	+4.5	+2.9	+2.3
Δ cap(+125°C)	%	+8.8	+5.0	+4.97	+7.90	+4.6	+4.8
		C.- Characteristics under life test (average of 10 capacitors)					
		Test according to CCTU O2-12B					
		C/40 V			C/50 V		
85°C–100%Vn(:)							
- after 2000 h							
Leakage	μAmp/capacitor	0.539	0.414	0.393	0.182	0.288	0.192
Breakdowns		0	0	0	0	0	0
- after 4000 h							
Leakage	μAmp/capacitor	0.747	0.446	0.368	0.414	0.300	0.260
Breakdowns		1	0	0	0	0	0
125°C-66%Vn(:)							
- after 2000 h							
Leakage	μAmp/capacitor	0.436	0.450	0.114	0.378	0.966	0.385
Breakdowns		0	0	0	1	0	0
- after 4000 h							
Leakage	μAmp/capacitor	0.867	0.623	0.235	0.247	0.440	0.269
Breakdowns		2	0	0	2	1	0
		D.- Characteristics under direct (positive) and reverse (negative) voltages (average of 5 capacitors)					
		C/40 V			BDV (+) C/40 V		
Leakage at					POSITIVE POLARIZATION OF TANTALUM		
+ 120 V	μAmp/capacitor	100		110	105 V		95 V
+ 80 V	μAmp/capacitor	0.4		4			
+ 30 V	μAmp/capacitor	0.1		0.4			
– 3 V	μAmp/capacitor	0.01		0.08	NEGATIVE POLARIZATION OF TANTALUM		
– 10 V	μAmp/capacitor	30		0.5			
– 20 V	μAmp/capacitor	1000		40	25 V		32 V
– 30 V	μAmp/capacitor	Breakdown		100			

(+) BDV = Breakdown voltage
(:) Vn = Nominal voltage

What we claim is:

1. A valve-metal base powder for use in electronics, the grains of which powder are made up of the said valve-metal containing between about 0.06 and about 2 percent by weight of at least one additive metal chosen in the group consisting of Mo, V, W, and Hf.

2. A valve-metal base powder for use in electronics, the grains of which powder are made up of a nucleus of the said valve-metal covered with a surface layer of the same valve-metal containing between about 0.01 and about 2 percent by weight of at least one additive metal chosen in the group consisting of No, V, W and Hf.

3. A powder as claimed in claim **2,** in which the thickness of the surface layer is lower than 3,000 Angstroms.

4. A valve-metal base powder for use in electronics, the grains of which powder are made up of a nucleus of the said valve-metal covered with a surface layer consisting of at least one metal chosen in the group consisting of Mo, V, W and Hf.

5. A powder as claimed in claim **4,** in which the thickness of the surface layer is lower than 3,000 Angstroms.

6. A powder as claimed in claim **1,** in which the said valve-metal is chosen in the group consisting of tantalum and niobium.

* * * * *