



US 20080233420A1

(19) **United States**

(12) **Patent Application Publication**
McCracken et al.

(10) **Pub. No.: US 2008/0233420 A1**
(43) **Pub. Date: Sep. 25, 2008**

(54) **PRODUCTION OF HIGH-PURITY
TANTALUM FLAKE POWDER**

(52) **U.S. Cl. 428/546; 75/354; 75/357**

(76) Inventors: **Colin G. McCracken**, Sinking Spring, PA (US); **Scott M. Hawkins**, Fleetwood, PA (US)

(57)

ABSTRACT

Correspondence Address:
DUANE MORRIS, LLP
IP DEPARTMENT
30 SOUTH 17TH STREET
PHILADELPHIA, PA 19103-4196 (US)

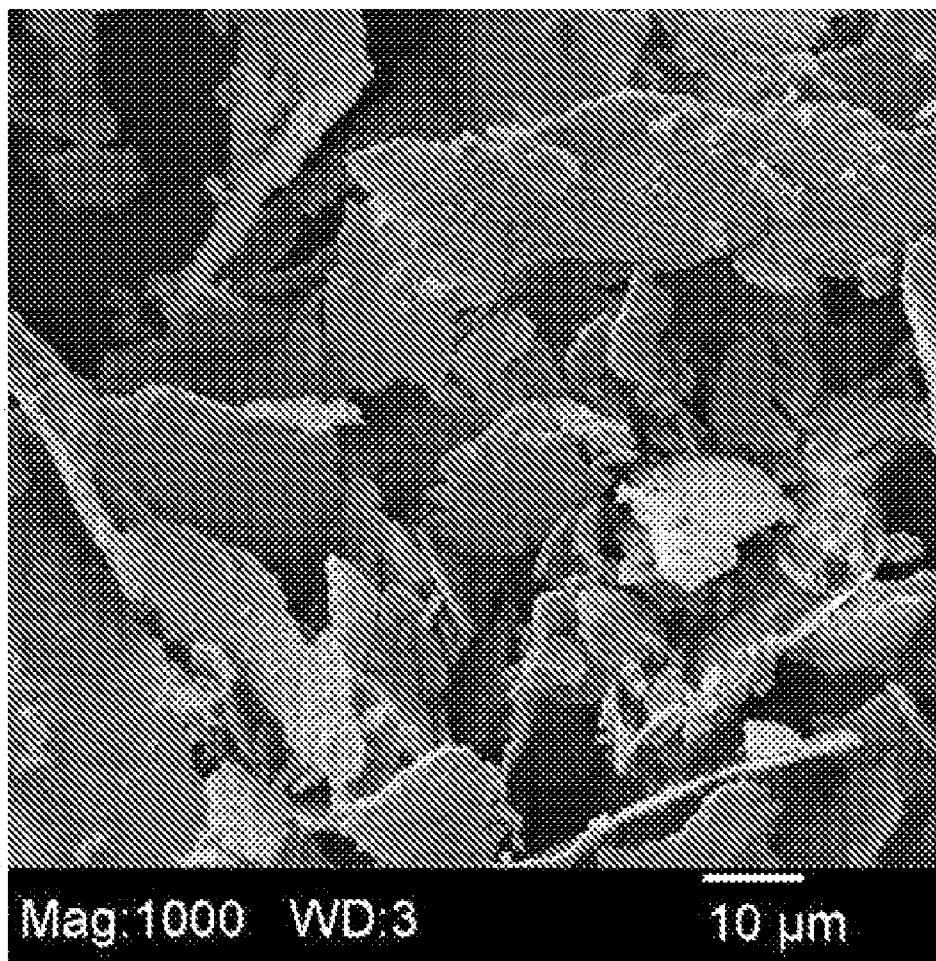
The present invention relates to a high-purity tantalum flake powder, produced by a hydride-dehydride process including: (a) cold working tantalum metal into a thin sheet; (b) hydriding the thin sheet, forming a brittle tantalum foil; (c) adjusting the tantalum foil to a desired particle size; and (d) removing hydrogen from the tantalum foil by vacuum sintering, forming a tantalum flake powder. In accordance with the present invention, tantalum flake is produced by sizing ultra-thin tantalum foil via the hydride-dehydride process. Tantalum is an extremely malleable metal and can be cold worked into extremely thin sheets less than 1 micron thick. Once hydrided, this foil is brittle, and can be easily sized by suitable milling processes. The hydrogen is removed by vacuum sintering, resulting in an extremely thin Ta metal flake.

(21) Appl. No.: **11/690,523**

(22) Filed: **Mar. 23, 2007**

Publication Classification

(51) **Int. Cl.**
C22B 34/24 (2006.01)
B22F 9/04 (2006.01)



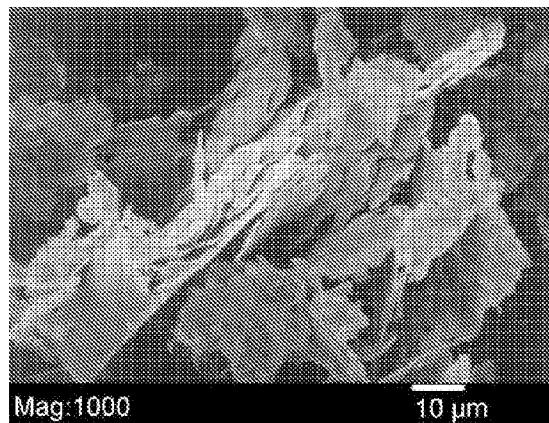


FIG. 1

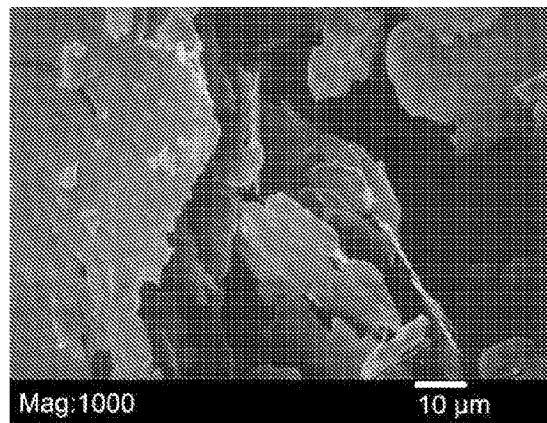


FIG. 2

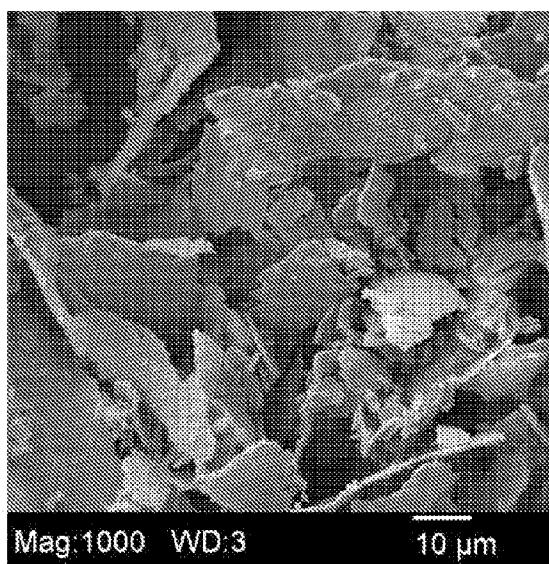


FIG. 3

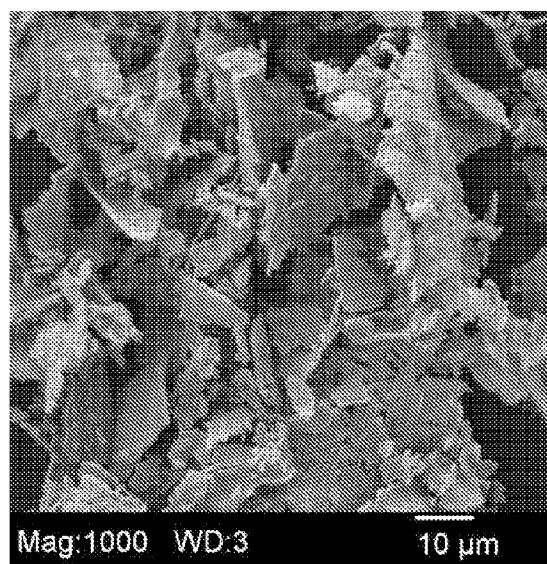


FIG. 4

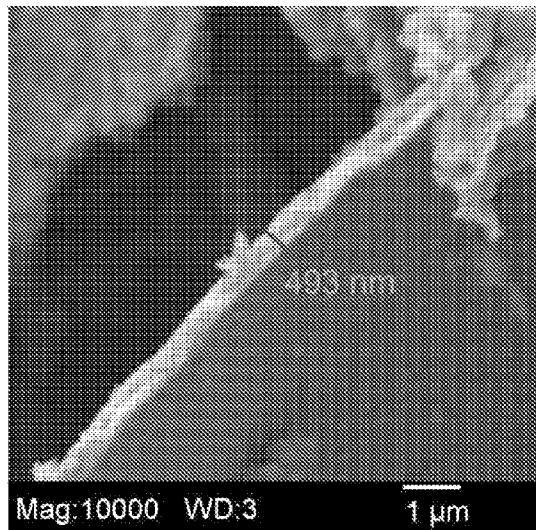


FIG. 5

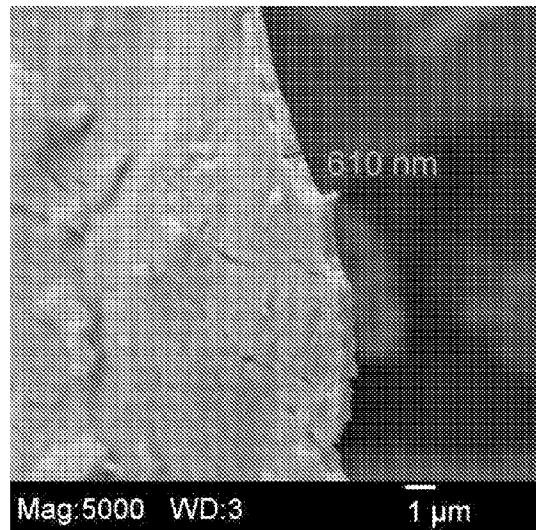


FIG. 6

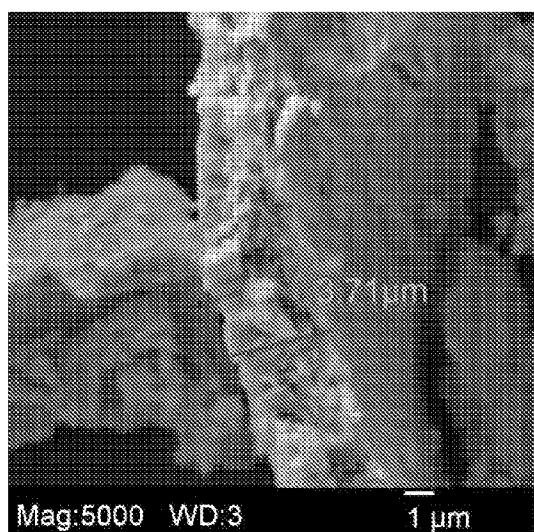


FIG. 7

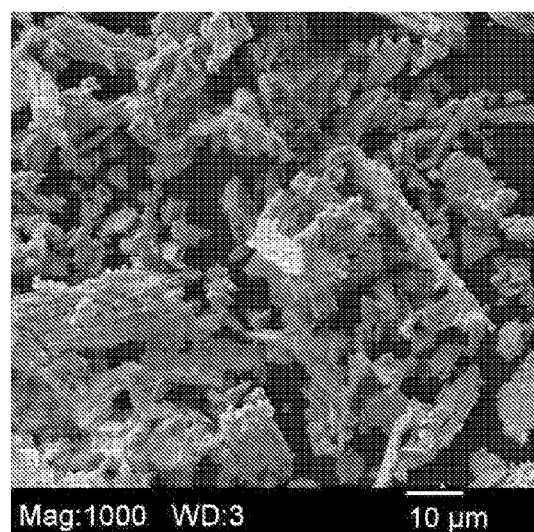
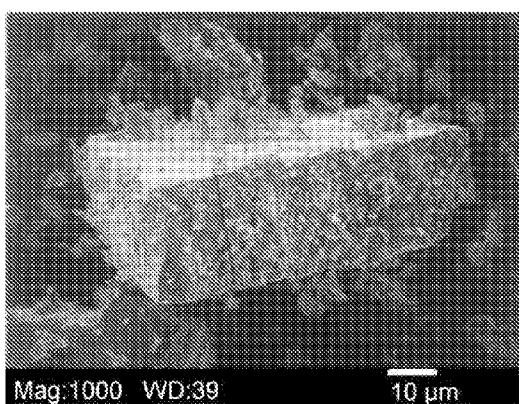


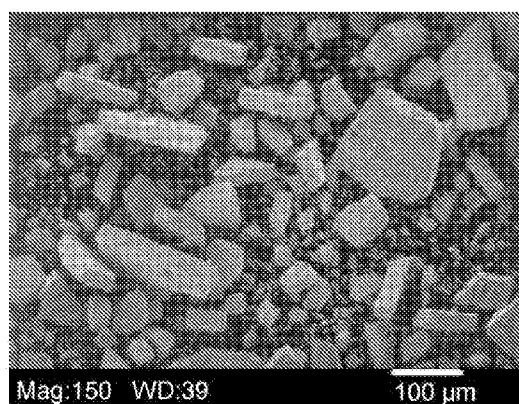
FIG. 8



Mag:1000 WD:39

10 μm

FIG. 9



Mag:150 WD:39

100 μm

FIG. 10

PRODUCTION OF HIGH-PURITY TANTALUM FLAKE POWDER

FIELD OF THE INVENTION

[0001] The present invention relates generally to methods of manufacturing tantalum flake for high CV/g/high voltage capacitors, using a process of mechanically flattening a nodular powder. Such an alternative method results in the production of tantalum flake with the potential for higher capacitance.

BACKGROUND OF THE INVENTION

[0002] Tantalum electrolytic capacitors date back to the late 1940's. Since that time, many improvements have been made to the manufacturing process, allowing for smaller, more reliable, and better performing components. Today, high CV/g/high voltage tantalum capacitors are dominated by flake technology. The particular flake morphology allows for high voltage applications, as the contacts between particles are line, rather than point with traditional powder metallurgy. As the dielectric is grown on the tantalum, it consumes a portion of the underlying metal. The thicker the dielectric, the more metal is consumed, resulting in thinner contacts between particles. The entire sinter neck eventually is consumed and the particles become electrically isolated. Flake morphology allows the dielectric to be formed to higher voltages before choking off the sinter necks between particles.

[0003] Currently, tantalum flakes are typically produced by mechanically flattening tantalum particles. The particles are either from tantalum EB ingots or from the reduction of K_2TaF_7 with Na metal in a molten salt reactor. The malleable metal particles are flattened in a high-energy ball mill before being hydrided and reduced in size by impact milling. In order to reduce contamination, the tantalum is usually ball milled in an organic solvent, and acid leached. A deoxidation step is needed to reduce the oxygen to suitable levels for capacitor use, and a heat treatment is then applied to produce the necessary physical properties such as flow, and Scott Density.

[0004] The mechanical flake process produces a distribution of particle thickness. This variation in flake thickness reduces the performance of the capacitor at a given formation voltage. Flakes thinner than a specific value will be completely choked off, while flakes thicker than that value will not, for a given forming voltage. Capacitor powder manufacturers are continually improving the manufacturing process, in an attempt to reduce distribution of flake thicknesses. The present invention relates to a process to produce tantalum flake suitable for use in high CV/g/high voltage capacitor applications that overcomes technical difficulties in existing processes.

SUMMARY OF THE INVENTION

[0005] The present invention relates to a high-purity tantalum flake powder, produced by a hydride-dehydride process comprising:

- [0006]** (a) cold working tantalum metal into a thin sheet;
- [0007]** (b) hydriding the thin sheet, forming a brittle tantalum foil;
- [0008]** (c) adjusting the tantalum foil to a desired particle size; and

[0009] (d) removing hydrogen from the tantalum foil by vacuum sintering, forming a tantalum flake (agglomerate) powder.

[0010] In accordance with the present invention, tantalum flake is produced by sizing ultra-thin tantalum foil via the hydride-dehydride (HDH) process. Tantalum is an extremely malleable metal and can be cold worked into extremely thin sheets less than 1 micron thick. Once hydrided, this foil is brittle, and can be easily sized by suitable milling processes. The hydrogen is removed by vacuum sintering, resulting in an extremely thin Ta metal flake. In embodiments, the hydriding occurs at a temperature of about 400-800° C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The accompanying drawings illustrate preferred embodiments of the invention as well as other information pertinent to the disclosure, in which:

[0012] FIGS. 1 and 2 are illustrations of tantalum flake produced by the prior art mechanical flake process;

[0013] FIGS. 3 and 4 are illustrations of dehydride tantalum flake produced by the process of the present invention, from 0.5 μm foil;

[0014] FIGS. 5 and 6 are further illustrations of dehydrided and hydrided tantalum flake, respectively, produced by the process of the present invention;

[0015] FIGS. 7 and 8 are illustrations of hydride tantalum flake produced by the process of the present invention, from 2.5 μm foil; and

[0016] FIGS. 9 and 10 are illustrations of hydride tantalum flake produced by the process of the present invention, from 25 μm foil.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] An advantage of the process of the present invention over the mechanical process is that the flakes produced have a much narrower thickness distribution. The final flake thickness is completely dependent on the foil thickness prior to hydriding. Foil thickness can be measured and selectively chosen to produce an extremely narrow finished flake thickness distribution. With the mechanical flake process, flakes that are too thick or too thin cannot be removed from the sample. The method of the present invention is an improvement in the mechanical flake process.

[0018] An additional advantage of the process of the present invention is the attainment of uniform thickness across the length of each individual flake. In other words, the flake is the same thickness at the center as it is at the edge. This is not the case with the mechanical flake process, where flakes tend to be much thinner at the edge than at the center. The advantage of a uniform flake thickness is more uniform, thicker sinter necks between particles.

[0019] Since the tantalum foil is cold rolled into thin sheets, the process of the present invention has the potential for lower levels of contamination than the mechanical flake process. Note that mechanical flake manufacturers mill tantalum in organic solvents to minimize contamination; a consequence is an increase in the carbon content of the finished material. Carbon is presumed to be a significant cause of field crystallization during the forming process, which leads to an increase in the leakage current of the capacitor. It is anticipated that the process of the present invention will result in a lower leakage current than the mechanical flake process.

pated that other contaminants will be lower with the flake process of the present invention, including oxygen.

EXAMPLES

[0020] Several sheets of Ta foil at various thicknesses and foil dimensions (150*500 mm, 50*50 mm and 25*25 mm) were tested, as shown in Table 1, below.

TABLE 1

Sample	Foil Thickness (μm)	Foil Dimensions (mm)
1	25	150 × 500
2	2.5	50 × 50
3	0.5	25 × 25

[0021] Foil samples 1 and 2 were hydrided in a large HDH vessel at 600° C. Sample number 3 was hydrided in a small HDH vessel at 600° C. after being annealed under vacuum at 900° C. for 24 hours. After hydriding, each sample was broken apart using a mortar and pestle. Images were taken on an ISI SR-50 Scanning Electron Microscope with secondary electron detector. Samples 2 and 3 were then dehydrated in a furnace at 700° C. and 600° C. respectively.

[0022] SEM images of the mechanical flake process are shown in FIGS. 1 and 2. These images show the flakes prior to hydriding, and final sizing. The finished flakes will be much smaller in size. Edges of the flakes appear sharp, and less than 1 micron thick. FIGS. 3 and 4 show dehydrate tantalum flake from the flake process of the present invention, at the same magnification. The foil used to produce these flakes was 0.5 μm thick (Sample 3). As shown in these images, the process of the present invention produces tantalum flakes very similar in size and shape to the mechanical flake process. By introducing a suitable classification process, most of the “fines” present in the material produced in accordance with the present invention could easily be removed.

[0023] As noted above, the process of the present invention results in more uniform thickness across the length of the individual flakes, which translates into thicker edges on the flakes. The edges of the flakes are typically where the sinter necks are formed. A thicker edge provides potential for thicker sinter necks. The SEM images of FIGS. 5 and 6 are high magnification flakes produced in accordance with the present invention, which show the well-defined edges. FIG. 5 shows dehydrate tantalum foil, while FIG. 6 shows hydrided tantalum foil. Both are from 0.5 μm foil (Sample 3). The difference in the thickness of the flakes is attributable to the difference in density between hydride and dehydrate. Tantalum hydride has a density of about 13.2 g/cm³, while tantalum metal has a density of 16.6 g/cm³; this represents a 26% difference in density, which corresponds to a 26% increase in the flake thickness from hydride to dehydrate. The measured thickness difference in the SEM images is 24%, which shows a good correlation to the theoretical.

[0024] Tantalum flake produced from thicker tantalum foil (Samples 1 and 2) were also imaged on the SEM. These images illustrate the dependence of the initial foil thickness on the final flake thickness. They also show that a hydrided tantalum foil is more likely to break perpendicular to the foil surface, rather than parallel to it. The first set of images (FIGS. 7 and 8), is hydrided tantalum flake from 2.5 μm thick tantalum foil (Sample 2). This sample was not annealed prior to being hydrided, as the 0.5- μm sample (Sample 3) was in FIGS. 3 and 4. The high surface stresses from the cold work-

ing, when not relieved by thermal annealing, tended to produce more irregular shaped flakes when sized as hydride, as shown in FIG. 8. The flake produced from the 25 μm foil does not have as much surface stress, and therefore produced more uniform flakes. The second set of images (FIGS. 9 and 10), are hydrided tantalum flake produced from 25- μm thick tantalum foil.

[0025] Chemical analysis from the foil samples is listed in Tables 2 and 3, below. While no carbon level is listed for the thinnest tantalum foil (0.5 μm), the level for the thickest (25 μm) is less than 10 ppm on the certificate of analysis. This level of carbon contamination is a significant improvement over the mechanical milling process. Minimal carbon pick-up is expected from the HDH, and sizing processes. Other contaminant levels listed on the respective certificates of analysis are low enough for use in electronic applications.

TABLE 2

Specifications for tantalum foil (0.5 μm thick)

Element	ppm
Al	5
Ca	2
Co	1
Cr	5
Cu	2
Fe	30
Mg	5
Mn	2
Mo	100
Na	10
Nb	<500
Ni	3
Si	10
Sn	2
Ti	20

TABLE 3

Specifications for tantalum foil (25 and 2.5 μm thick)

Element	ppm
C	<10
Fe	4
H	<5
Mo	<2
N	<10
Nb	10
Ni	<1
O	14
Si	<10
Ti	<1
W	<1

[0026] Thus, in accordance with the present invention, tantalum flake suitable for use in high CV/g/high voltage capacitor applications can be manufactured by hydriding and sizing very thin tantalum foil, where the initial foil thickness determines the final flake thickness. Hydrogen can later be removed by vacuum annealing.

[0027] There are several advantages to using foil over mechanically flattening tantalum particles. First, it produces a very narrow flake thickness distribution. The thickness of the flakes determines the maximum forming voltage of the material. A higher formation voltage corresponds to a thicker dielectric oxide and higher breakdown voltages. With a narrow thickness distribution, fewer flakes will be formed

through for a given voltage, increasing the material's CV/g. In order to optimize the performance of the material, capacitor manufacturers desire the highest formation voltage possible, without electrically isolating particles by consuming the underlying metal during forming.

[0028] Secondly, more uniform thickness across the length of the flake is produced. This can be seen in the sharp, well-defined edges of the flakes (see e.g., FIGS. 5 and 6). Since particles typically sinter at the edges, a thicker edge means thicker sinter necks. Furthermore, contaminant levels are lower in the flake process of the present invention, particularly carbon. It is hypothesized that a major cause of field crystallization during forming is a result of carbon contamination on the particle surface. Since the flake process of the present invention does not use any organic solvents during processing, carbon contamination is much lower than the mechanical flake process. This should result in lower leakage current in the finished capacitors, another advantage over the mechanical process.

[0029] While the present invention has been described with respect to particular embodiment thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications, which are within the true spirit and scope of the present invention.

What is claimed is:

1. A high-purity tantalum flake powder, produced by a hydride-dehydride process comprising:
 - (a) cold working tantalum metal into a thin sheet;
 - (b) hydriding the thin sheet, forming a brittle tantalum foil;
 - (c) adjusting the tantalum foil to a desired particle size; and
 - (d) removing hydrogen from the tantalum foil by vacuum sintering, forming a tantalum flake powder.
2. The tantalum flake powder as recited in claim 1, wherein the flake is of a uniform thickness across its length.
3. The tantalum flake powder as recited in claim 1, wherein the flake has a thicker sinter neck.
4. The tantalum flake powder as recited in claim 1, wherein the hydriding occurs at a temperature of about 400-800° C.

5. The tantalum flake powder as recited in claim 4, wherein the hydriding occurs at a temperature of about 600° C.

6. The tantalum flake powder as recited in claim 1, wherein the brittle tantalum foil has a thickness of about 0.5-25 µm.

7. The tantalum flake powder as recited in claim 1, wherein the presence of contaminants in the powder is minimized.

8. The tantalum flake powder as recited in claim 1, wherein electronic valves are produced from tantalum flake powders.

9. The tantalum flake powder as recited in claim 1, further comprising screening the tantalum flake powder to a final particle size distribution.

10. A method of producing tantalum flake powder which comprises:

- (a) cold working tantalum metal into a thin sheet;
- (b) hydriding the thin sheet, forming a brittle tantalum foil;
- (c) adjusting the tantalum foil to a desired particle size; and
- (d) removing hydrogen from the tantalum foil by vacuum sintering, forming a tantalum flake powder.

11. The tantalum flake powder as recited in claim 10, wherein the flake is of a uniform thickness across its length.

12. The tantalum flake powder as recited in claim 10, wherein the flake has a thicker sinter neck.

13. The tantalum flake powder as recited in claim 10, wherein the hydriding occurs at a temperature of about 400-800° C.

14. The tantalum flake powder as recited in claim 13, wherein the hydriding occurs at a temperature of about 600° C.

15. The tantalum flake powder as recited in claim 10, wherein the brittle tantalum foil has a thickness of about 0.5-25 µm.

16. The tantalum flake powder as recited in claim 10, wherein the presence of contaminants in the powder is minimized.

17. The tantalum flake powder as recited in claim 10, wherein electronic valves are produced from tantalum flake powders.

18. The tantalum flake powder as recited in claim 10, further comprising screening the tantalum flake powder to a final particle size distribution.

* * * * *