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(54) **Title:** METHOD FOR THE PRODUCTION OF TANTALUM POWDER USING RECLAIMED SCRAP AS SOURCE MATERIAL

(57) **Abstract:** A process for obtaining tantalum powder from tantalum containing scrap material is provided. The process includes selecting source material, such as from sintered anodes for capacitors, hydriding the source material, milling to desired particle size and surface area, dehydriding, deoxidizing, agglomerating, sifting, and acid treating to obtain tantalum powder of a desired size and purity.

Method for the Production of Tantalum Powder Using Reclaimed Scrap as Source Material

Cross Reference to Related Application

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 60/979,949, filed October 15, 2007, the entirety of which is hereby incorporated by reference into this application.

Field of the Invention

[0002] The invention relates to metal tantalum powder. More particular the invention relates to processes for the production of tantalum powder

Description of the Related Art

[0003] Capacitors have been produced from tantalum powder for many years. For example, tantalum powder may be manufactured by molten sodium reduction of potassium heptafluorotantalate, K_2TaF_7 which is produced by digesting tantalum ore or tantalum scrap in hydrofluoric acid, separating the tantalum values by solvent extraction and precipitating K_2TaF_7. Another method involves milling of hydrided ingot. The ingots are typically melted in an electron beam furnace under vacuum to achieve the very high melting temperature of tantalum, about 3000°C.

[0004] Such conventional methods are expensive. Additionally, the use of hydrofluoric acid poses a hazard to technicians and equipment. Improvements to the process for producing tantalum powder are constantly desired in the marketplace. Tantalum capacitors are used for a wide range of applications from very high reliability military and medical applications to commercial applications and consumer electronics.

[0005] It would be desirable to have a more cost effective method to produce tantalum powder. It would be desirable to have a method and process to produce

commercial grade capacitor powder from reclaimed tantalum scrap that does not require hydrofluoric acid digestion or re-melting the material into ingots.

Summary of the Invention

[0006] Methods for converting processed tantalum source material into usable capacitor grade powder are described. The material may be from a variety of sources but is preferably from tantalum scrap. Such tantalum scrap includes tantalum anodes made from sintered powder, deoxidized tantalum anodes or from other high purity tantalum scrap such as fabricated sheet made from ingot.

[0007] The use of scrap material to obtain tantalum powder presents several challenges as compared to virgin material, including the presence of varying amounts of impurities, some of which must be removed prior to processing. The powder is prepared by first sorting material, removing contaminants below acceptable levels, processing to achieve the desired surface area and then further treating to form an agglomerated capacitor powder.

[0008] The invention has many advantages over conventional processes to obtain tantalum powder. Commercial grade capacitor powder from tantalum scrap is obtained by the inventive processes without using hydrofluoric acid digestion or having to initially or subsequently re-melt the source material to ingots. The elimination of the these steps from conventional processes is significantly more economical, saves time and reduces the considerable hazards associated with chemicals such as hydrofluoric acid.

[0009] In one embodiment method for producing tantalum powder from tantalum containing source material is provided. The method comprises the steps of hydriding the source material, crushing and milling the hydrided source material to form a powder, dehydiding and agglomerate the powder to form agglomerates,

deoxidize the agglomerated powder; and optionally crushing and sifting the agglomerates to a desired particle size. Optionally, the method includes additional steps depending on the source material and the requirements of the final powder. These steps include, among others, acid treating the deoxidized crushed agglomerated powder, crushing and sifting the deoxidized crushed agglomerated powder to a desired particle size, treating the scrap material to remove contaminates prior to the step of hydriding the scrap material.

[00010] In one embodiment the step of crushing and milling the hydrided scrap forms a powder with a surface area between about 0.5 and 2.0 m^2/g. In another embodiment the agglomerates are formed of about 100 microns. The agglomerates may be crushed and sifted prior to the step of deoxidizing the agglomerates. The step of deoxidizing the agglomerated powder may be performed by mixing the agglomerates with Magnesium metal and heating under an inert gas.

[00011] The tantalum containing source material can be in a variety of forms. In one embodiment the tantalum scrap comprises tantalum capacitor anodes and/or manufacturing scrap from sheet and wire.

[00012] A method is provided of producing powder from reclaimed capacitor anodes that are sintered tantalum powder around a central tantalum wire. The method includes the steps of hydriding the material by heating the material in vacuum then backfilling with hydrogen, lightly milling the hydrided anodes to liberate the tantalum wire, sifting the milled anodes to separate the tantalum wire from the powder, heat treating the powder in two or more steps to dehydride, deoxidize, and agglomerate the powder and crushing the agglomerates and sifting to produce a particle size distribution capable of being pressed and sintered to re-form capacitor anodes.

[00013] Optionally, the initial steps of sampling the anodes to determine initial contamination levels and acid leaching the anodes to remove metallic contamination is performed. The acid treated anodes are then rinsed to remove acid residue and the rinsed anodes are dried. In an another embodiment the step of removing the oxide layer by heating with Mg at sufficient temperature and time to at least partially remove the oxide layer before the step of hydriding is included.

Detailed Description of the Invention

[00014] A process for obtaining tantalum powders from selected source material is provided. The source material must have a high concentration of tantalum but need not be in the form of ingots as is required by conventional techniques. The selection of source material is based on the form of the material and the amount and type of chemical contamination. The source material is thin, preferably less than about 2 mm, such as sheet or wire. Thin source material allows for easier and more complete hydriding. Acceptable forms include, but not limited to, thin sheet, sintered powder compacts (anodes), de-oxidized anodized anodes from capacitors and wire.

[00015] One preferred source material is tantalum scrap, such as various recycled tantalum materials including tantalum capacitor anodes, manufacturing scrap from high purity sheet and wire as well as other high purity tantalum scrap. One important feature of the invention is that the form of the source material need not be altered or changed to any specific form prior to treatment. For example, when the tantalum source material is scrap, the scrap need not be digested with HF acid and ultimately reduced with molten Sodium metal to form powder, or alternately melted at 3000°C in an electron beam furnace to form ingots, both of which processes have high associated costs as well as hazards.

[00016] Once selected, the source material is subjected to a process that includes a number of steps to produce the tantalum powder. In one embodiment, the selected source material is initially chemically treated to remove contaminants. The specific treatment depends on the specific contaminates present in the scrap and also depends on the desired purity of the final tantalum powder. For example, for many contaminates, the contamination can be leached or dissolved to sufficiently low levels by conventional means such as acid leaching in Hydrochloric, Nitric, or Sulfuric Acid or combinations of these acids, with or without additional oxidizing agents.

[00017] The treatment will also depend on the desired purity of the finished tantalum powder. In some instances, if the starting source material is of sufficient purity in relation to the desired final powder, no initial treatment is required. Those skilled in the art will readily be able to determine what treatment is necessary for the intended source material.

[00018] The source material is then hydrided using conventional techniques. For example, source material is heated in vacuum and then backfilled with Hydrogen. Hydriding makes the source material brittle and more easily crushed and milled, which is the next step in the process. Those skilled in the art will readily be able to determine an operative temperature/time profile to yield a high degree of Hydrogen uptake. Generally, the greater the Hydrogen uptake, the more brittle the source material and the easier it is to mill. The thicker the source material, the more difficult it becomes to hydride as there is typically a gradient of Hydrogen concentration from the surface to the interior of thick pieces.

[00019] Once hydrided, the hydrided material is crushed and milled to a powder. The equipment used for crushing and milling is that typically used for milling

metal. The specific process for crushing and milling the material will depend on the desired properties for the finished powder. For example, if the finished powder is intended to be commercial grade tantalum powder for, then the hydrided material is preferably milled to a fine powder with a relatively high surface area between about 0.5 and about 2.0 m^2/g. By "commercial grade," it is generally understood to mean non-military, usually consumer products requiring a lower degree of reliability and a wider operating specification. For example handheld devices: cell phones, games, etc are included in consumer grade applications. The finer the powder the more capacitance per gram, CV/g., which is one of the major price factors in Ta powder.

[00020] The crushed and milled powder is then dehydrided. Preferably the Tantalum is heated to about 1300° F, in a vacuum to dehydride the powder. Under the right conditions the dehydrided powder will agglomerate to produce agglomerates. For example, if the temperature is then increased to 2000° F agglomeration will occur. Such agglomerates will typically be of about 50 microns to about 250 microns; preferably the agglomerates are about 100 microns as these agglomerates have good flow characteristics, which is important for filling the small molds used to press the powder into anodes.

[00021] The agglomerated powder is then optionally crushed and sifted to remove undersized and oversized material thereby obtaining a sifted powder. This step is done to improve the uniformity of the powder. Again uniformity of material size is an important property when the powder is to be used for producing anodes. In other instances when uniformity is not as critical, the powder need not be crushed or sifted.

[00022] Preferably, the sifted powder is subsequently deoxidized. This is done to lower the oxygen content in the powder. In many common applications of

tantalum powder, it is desirable to minimize the amount of dissolved oxygen in the tantalum powders. In one embodiment, deoxidizing the powder is performed by mixing the powder with magnesium metal and heating under inert gas at elevated temperature, such as about 1,200 °F to about 1,600 °F, preferably about 1,450 °F. In many instances when high purity is desired, the deoxidized powder is acid treated, such as for example with warm Hydrochloric, Sulfuric Acid and Peroxide, Nitric Acid and Hydrochloric, or Niric Acid and Hydroflouric. This removes the magnesium and other metallic impurities added during milling and deoxidizing.

[00023] The deoxidized and acid treated powder is again crushed and optionally sifted to a desired particle size to obtain a tantalum powder. In one embodiment, the powder is crushed and sifted to a particle size of about 1.0 m^2/g, as this size is readily obtainable, easily deoxidized, and produces a good CV/g in the 15k to 30k range.

[00024] In alternate embodiments of the invention, one or more optional steps are included for producing tantalum powder from a tantalum containing source material. The specific form of the source material and the specific content and concentration of contaminates often require different steps to produce tantalum powder.

[00025] For example, in one embodiment, the source material includes reclaimed capacitor anodes comprising sintered tantalum powder around a central tantalum wire. In this embodiment, the process includes testing and selecting the source material. Samples of source material are tested to determine initial contamination levels of the source material. The testing is done by conventional testing methods known to those skilled in the art. The testing may reveal that certain samples contain too much of a particular contaminate and therefore not used.

[00026] For example, high levels of Nb, W, or Si are difficult to remove and therefore, materials containing these contaminates are typically not suitable for most applications. For another example, high levels of Mo typically require further testing to determine if the Mo is on the surface only, or in the interior of the material. For another example, high levels of Carbon also require further testing to determine the most effective removal efficiency. Most other normally present contamination can be removed by conventional methods know to those in the art. Depending on the results of the testing, the material may be subjected to acid leaching to remove metallic contamination identified in the testing. If acid treated, the material is then rinsed to remove acid residue and then dried.

[00027] The dried material is hydrided as described above, for example by heating the material in vacuum then backfilling with hydrogen. The hydrided material is milled, preferably light milling to liberate any tantalum wire. Tantalum wire typically contains a high silica content. If the wire does have high silica content, it is preferably separated from the powder so as not to contaminate the powder. The wire can be separated from the usable powder by sifting. The powder is heat treating to dehydride, deoxidize, and agglomerate the powder. The heat treatment is preferably performed in one or more steps, such as in two or more steps, or in several steps.

[00028] In one embodiment the steps of dehydriding, deoxidizing, and agglomerating is performed in a single step. The hydrided powder is pre-blended with Magnesium and put in a vacuum oven. A vacuum of about (7.5×10^{-4} Torr) is pulled and heated to 1300F until outgassing stops (dehydriding). The heat is increased to a temperature of about 1650° F for about 3 hours (deoxidizing) and then increased to about 2000°F-2400°F for about 30 minutes (agglomerating).

[00029] Finally the agglomerates are crushed and optionally sifted to produce a particle size distribution capable of being pressed and sintered to re-form capacitor anodes.

[00030] In a further embodiment, the source material is capacitor anodes that have been anodized. The anodized capacitor anodes have an oxide film which serves as a dielectric between the anode and the cathode in tantalum capacitors. The oxide film must be removed to a sufficient degree prior to the step of hydriding. In this further embodiment, the process for making metal powder from this type of source material may comprise the step of removing the oxide layer from the anodized capacitor anodes. This can be accomplished by heating the capacitor anodes with magnesium for a sufficient temperature and time to remove enough of the oxide layer to permit hydriding during the hydriding step. This step may be performed as a preprocessing step discussed above, or may be performed at any point in the process prior to the hydriding step discussed above.

[00031] In another aspect of the invention, a process is provided to manufacture tantalum powder from source material that is thin sheet. For example, the source material may be a thin sheet formed by rolling pure tantalum ingot into sheet material. Preferably, such sheet material has a thickness less than about 15 mm, and more preferably less than about 5 mm, and most preferably in a range from about 0.001 mm to about 5 mm.

[00032] The tantalum powder reclaimed through the processes described herein is can produce high quality powder such as that acceptable for use as sintered anodes for capacitors. As such, the processes may be adapted to produce agglomerated capacitor powder. Application of the processes described herein to

obtain tantalum powder having properties, such as size and purity, for applications other than to capacitors are also within the scope of the invention.

[00033] The following Examples are provided to illustrate embodiments of this invention. Other specific applications of the teachings in this patent application can be used without departing from the spirit of this invention. Other modifications of the methods can be used, and are considered to be within the scope of this invention.

[00034] Example 1

[00035] 25 kg of sintered, not anodized, gray anodes were washed to remove carbon residue, acid treated in 50% HNO_3 followed by HCl to remove metallic contamination. Subsequently the anodes were thoroughly rinsed and dried. The clean anodes were then sampled and analyzed. The results are provided in Table 1.

[00036] Table 1

Contaminate	Concentration
C	65 ppm
Cr	15 ppm
Fe	133 ppm
Mn	1 ppm
N	77 ppm
Ni	<10 ppm
O	0.318%
Zr	<1 ppm

[00037] The sample was hydrided by backfilling a vacuum oven to a positive pressure with Hydrogen at 482°C for 3 hours. The hydrided sample was wet milled with tantalum media for 30 minutes then sifted to separate the Ta wire from the

remaining material. The remaining material was milled for an additional 6 hrs to form a powder. The powder was rinsed and dried at 100°C for 24 hours. The powder was tested with a Fischer SubSieve Sizer and had a particle size of 1.1µm and a BET surface area of 1.1 m^2/g.

[00038] This powder was then dehydrided at 700°C and agglomerated at 1300°C for 30 minutes. The resulting agglomerates were crushed, sifted to -80 mesh, blended with Mg turnings and deoxidized at 900°C for 6 hours.

[00039] The resulting power was acid treated with 50% HNO_3 followed by conc. HCl to remove residual Mg. The powder was then rinsed and dried and then tested for particle size distribution. The mean diameter was 45 µm with 94% being 100µm or less. The powder was pressed and sintered and tested for wet leakage. At 60 V the anodes had a wet leakage of 1.5 nA/CV.

[00040] Example 2

[00041] 25 kg of thin Tantalum Sheet with an average thickness of 2 mm and a starting Oxygen content of <100 ppm was hydrided and milled as in Example 1. The final particle size and BET surface area was 2.5 µm and 0.79 m^2/g respectively.

[00042] There will be various modifications, adjustments, and applications of the disclosed invention that will be apparent to those of skill in the art, and the present application is intended to cover such embodiments. Accordingly, while the present invention has been described in the context of certain preferred embodiments, it is intended that the full scope of these be measured by reference to the scope of the following claims.

What is claimed is:

1. A method for producing tantalum powder from tantalum containing source material comprising the steps of:

hydriding the source material;

crushing and milling the hydrided source material to form a powder;

dehydiding and agglomerate the powder to form agglomerates;

deoxidize the agglomerated powder; and,

optionally crushing and sifting the agglomerates to a desired particle size.

2. The method of claim 1 further comprising the step of acid treating the deoxidized crushed agglomerated powder.

3. The method of claim 1 further comprising the step of crushing and sifting the deoxidized crushed agglomerated powder to a desired particle size.

4. The method of claim 1 further comprising the step of treating the scrap material to remove contaminates prior to the step of hydriding the scrap material.

5. The method of claim 1 wherein the step of crushing and milling the hydrided scrap form a powder with a surface area between about 0.5 and 2.0 m^2/g.

6. The method of claim 1 wherein agglomerates are formed of about 100 microns.

7. The method of claim 1 further comprising the step of crushing and sifting the agglomerates prior to the step of deoxidizing the agglomerates.

8. The method of claim 1 wherein the step of deoxidizing the agglomerated powder is performed by mixing the agglomerates with Magnesium metal and heating under an inert gas.

9. The method of claim 1 where the tantalum containing source material is tantulam scrap comprising one or more of Tantalum capacitor anodes and manufacturing scrap from sheet and wire.

10. The method of claim 1 further comprising the step of identifying impurities in the source material prior to the step of hydriding the source material.

11. The method of claim 1 further comprising the step of removing impurities prior to the step of hydriding the source material.

12. The method of claim 11 further wherein the impurities are removed by acid treating the source material.

13. A method of producing powder from reclaimed capacitor anodes that are sintered tantalum powder around a central tantalum wire comprising the step of:

hydriding the material by heating the material in vacuum then backfilling with hydrogen;

lightly milling the hydrided anodes to liberate the tantalum wire;

sifting the milled anodes to separate the tantalum wire from the powder;

heat treating the powder in one or more steps to dehydride, deoxidize, and agglomerate the powder; and

crushing the agglomerates and sifting to produce a particle size distribution capable of being pressed and sintered to re-form capacitor anodes.

14. The method of claim 13 further comprising the initial steps of sampling the anodes to determine initial contamination levels and treating the anodes to at least partially remove the contamination.

15 The method of claim 14 wherein the treating the anodes is done by acid leaching the anodes.

16. The method of claim 13 further comprising the steps of rinsing the acid treated anodes to remove acid residue and drying the rinsed anodes.

17. The method of claim 13 further wherein the capacitor anode contains a oxide film and further comprising the step of removing the oxide layer by heating with Mg at sufficient temperature and time to at least partially remove the oxide layer before the step of hydriding.

18. The method of claim 1 further comprising the initial steps of sampling the source material to determine initial contamination levels and treating the source material to remove contamination.

19. The method of claim 18 wherein the treating the source material is done by acid leaching the source material.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/079330

A. CLASSIFICATION OF SUBJECT MATTER

B22F 9/20(2006.01)i, B22F 1/00(2006.01)i, H01G 9/052(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC B22F 1/00, B22F 1/04, B22F 3/00, B22F 3/20, B22F 9/02, B22F 9/04, B22F 9/20, B22F 9/22, B22F 9/30, C22C 27/00, C22C 27/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applications for Utility models since 1975

Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS (KIPO internal) & keywords: tantalum powder, hydriding, dehydriding, deoxidizing, and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4740238 A (EDWARD K. SCHIELE) 26 April 1988 See the abstract; figure 1; and column 2, lines 12-59	1-19
A	US 4141719 A (JAMES B. HAKKO) 27 Februry 1979 See the abstract; figure 1; and claims 1-14	1-19
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A	KR 10-2004-0090982 A (H.C. STARCK, INC.) 27 October 2004 See the abstract; and claim 1	1-19
A	JP 2007-107056 A (OSAKA PREFECTURE UNIV.) 26 April 2007 See the abstract; and claims 1, 2	1-19

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 MARCH 2009 (06.03.2009)	**10 MARCH 2009 (10.03.2009)**

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/079330

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The common technical feature among independent claims 1 and 13 is 'a method for producing tantalum powder comprising the steps of: hydriding, milling, dehydriding, agglomerating, and deoxidizing'. However, this feature is not considered the "special technical feature" because it lacks an inventive step with respect to document US 4740238 A cited in the ISR. Hence, there is a lack of unity "a posteriori" (PCT Rules 13.1 and 13.2).

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2008/079330

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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