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(54) Producing tantalum or columbium powder

(57) Production of tantalum or columbium powder with a high yield of within a described range of particle sizes is disclosed. A molten salt bath of a double salt comprising either an alkali metal tantalum fluoride or an alkali metal columbium fluoride and a relatively large amount of alkali metal halide diluent salt to act as a heat sink is initially maintained at a temperature a little above the liquidus temperature of the salt mixture. A liquid alkali metal at a comparatively low temperature is

added to the continuously stirred bath at a high mass flow rate, and reduces the double salt, producing tantalum or columbium. The reaction is exothermic and causes the temperature to rise rapidly to a desired final reaction temperature within the range 760 - 1000°. The liquid alkali metal is thereafter fed at a high mass flow rate to complete the reaction quickly at the final reaction temperature. Forced cooling at a heat extraction rate ≤ 42 kilojoules/min./kg. of double salt is used during at least a portion of the reaction cycle at a rate sufficient to maintain the final reaction temperature within a desired range.

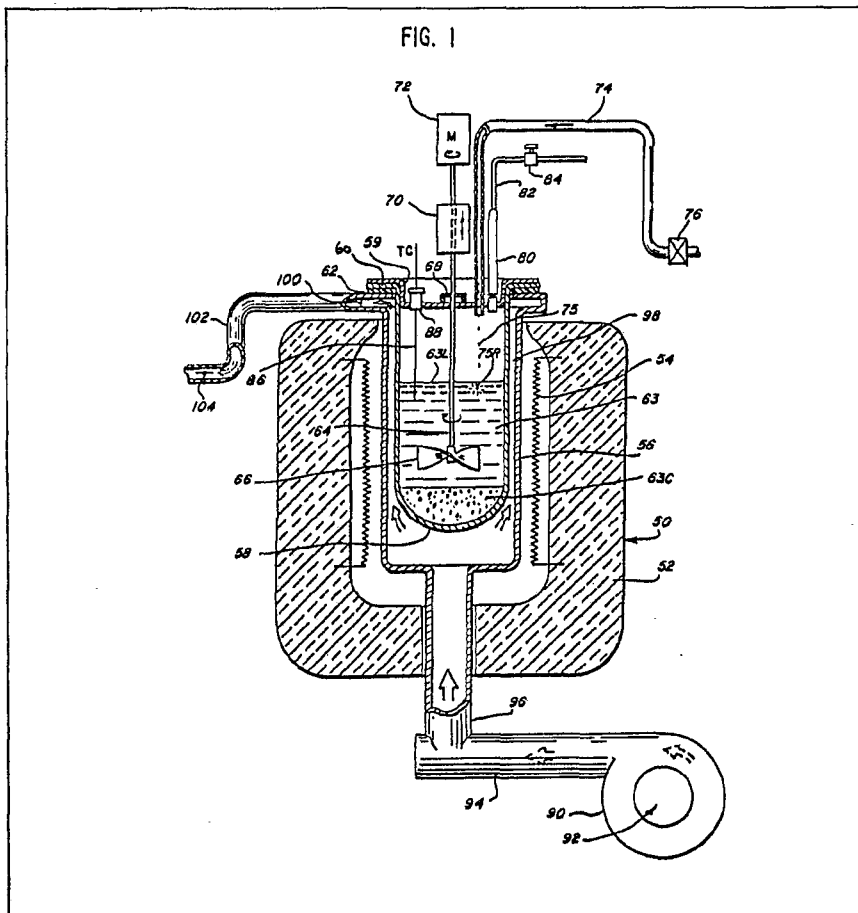
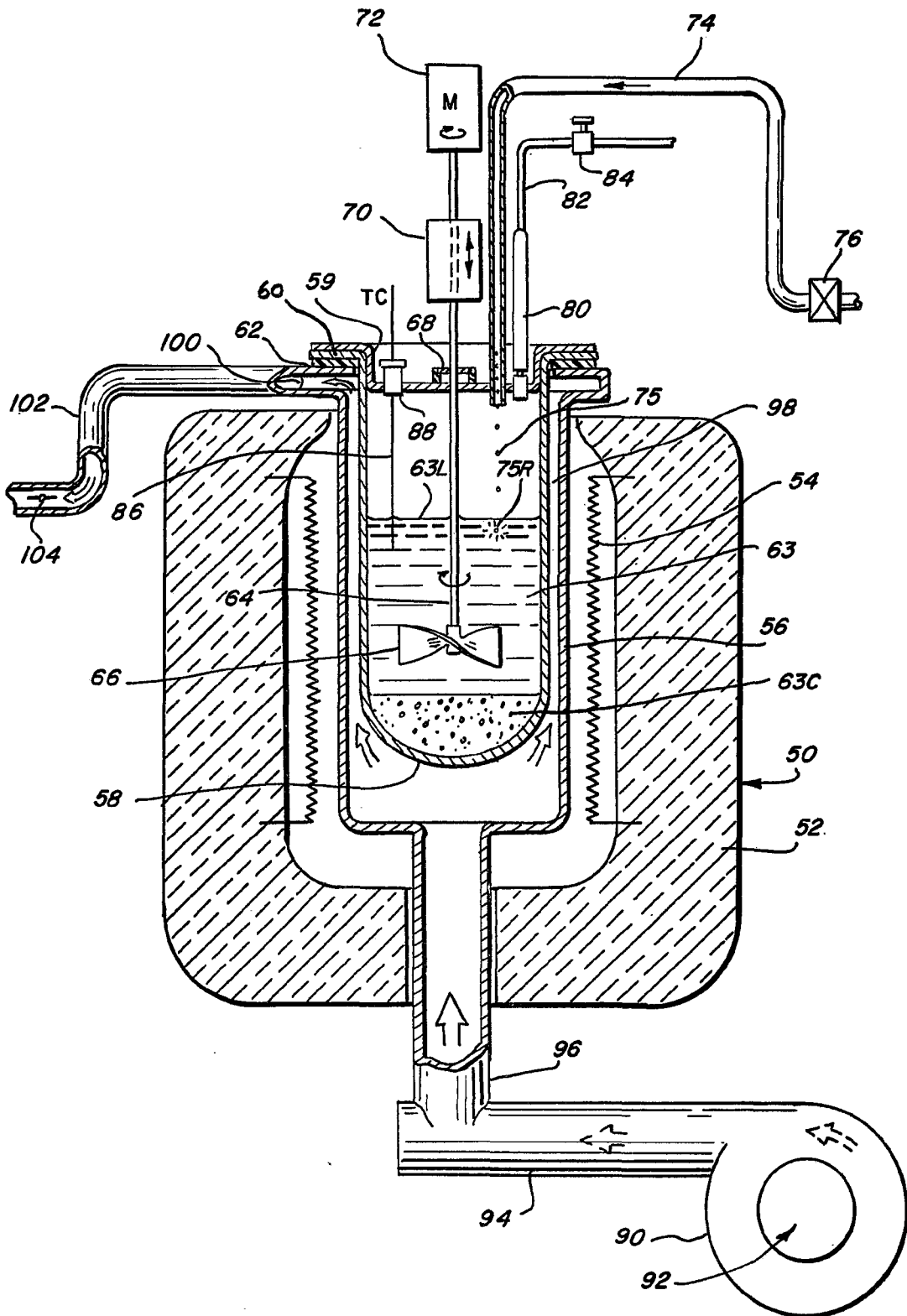


FIG. 1



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FIG. 2

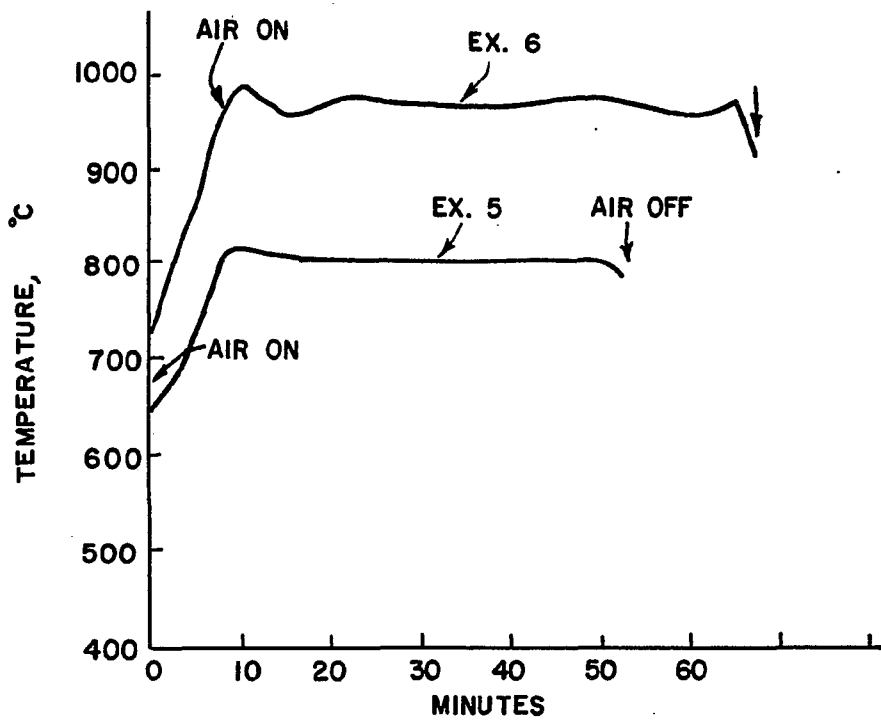
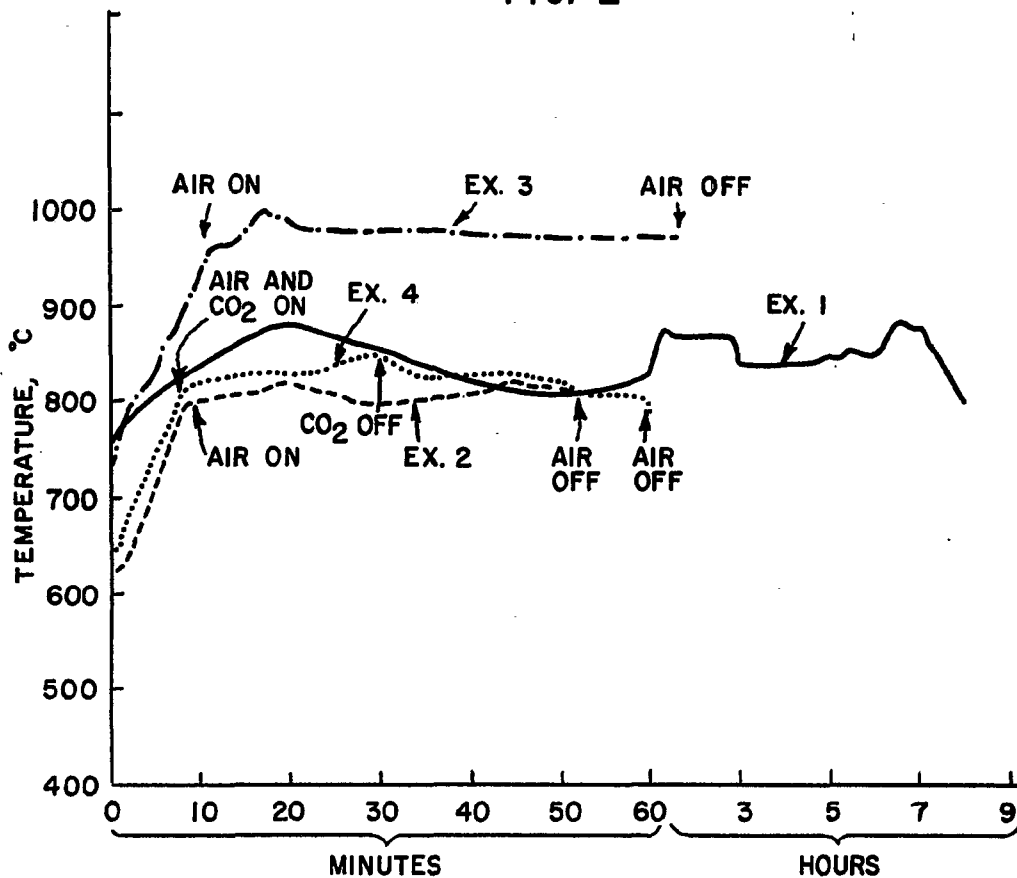
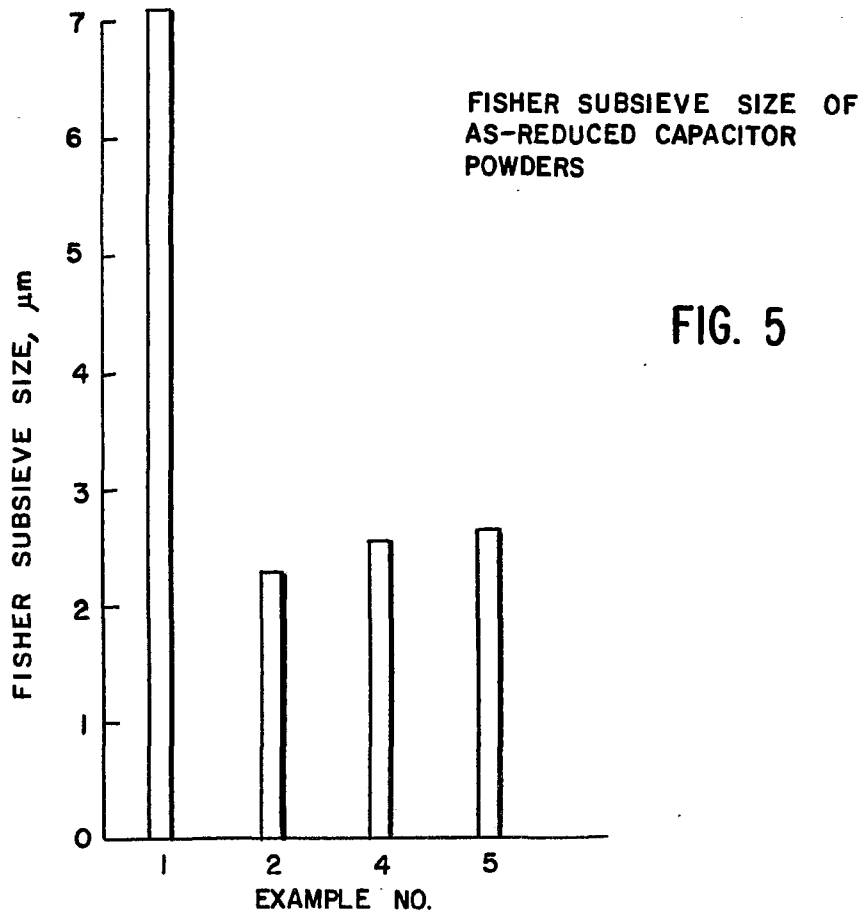
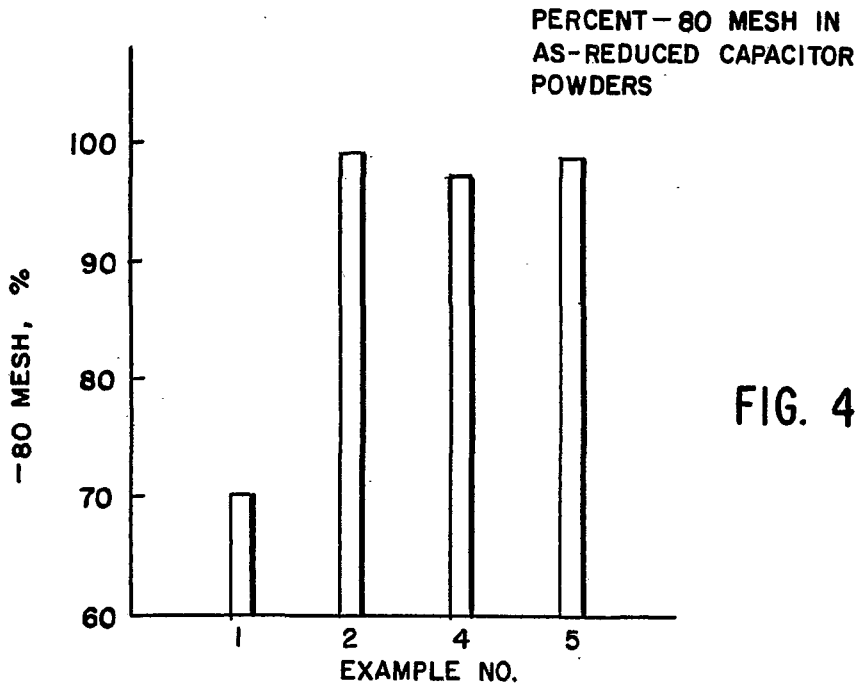
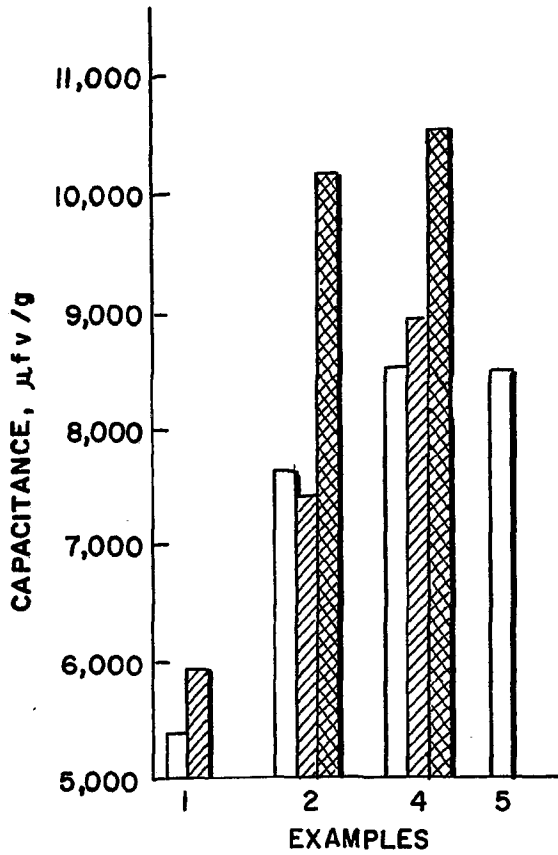


FIG. 3

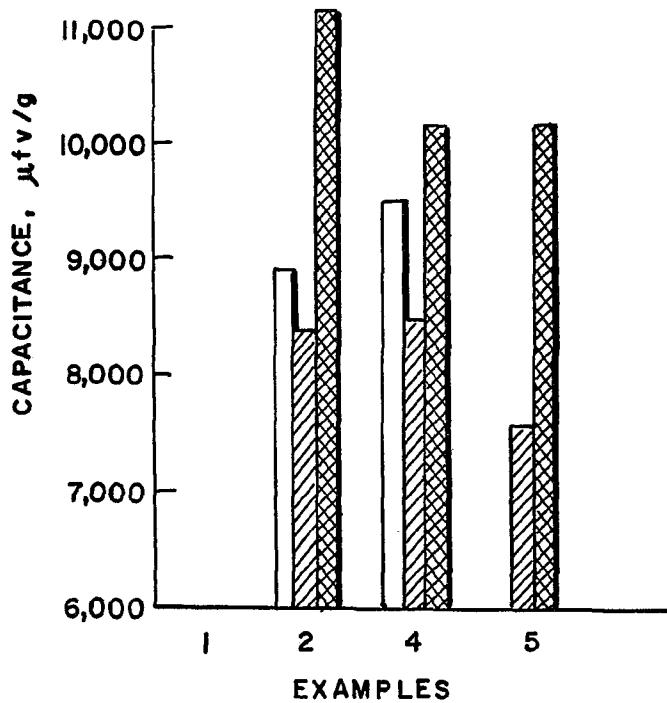
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CAPACITANCE OF 1.0-g ANODES PRESSED TO A GREEN DENSITY OF 6.45 g/cm³ FROM AS-REDUCED, THERMALLY AGGLOMERATED, AND PHOSPHORUS-DOPED TANTALUM POWDERS (ANODES SINTERED 30 MIN. AT 1600°C)

FIG. 6



CAPACITANCE OF 1.0-g ANODES PRESSED TO A GREEN DENSITY OF 5.5 g/cm³ FROM AS-REDUCED, THERMALLY AGGLOMERATED, AND PHOSPHORUS-DOPED TANTALUM POWDERS (ANODES SINTERED 30 MIN. AT 1600°C)

FIG. 7

SPECIFICATION

Process for producing tantalum and columbium powder

5 This invention relates to the production of tantalum and columbium powders. These metal powders have the characteristic of producing very high capacitive charge anodes for the manufacture of electrolytic capacitors. According to one aspect of the invention, a process for producing a tantalum or columbium powder comprises maintaining a liquid bath of a double salt of the formula:

10 R_2MX_7 10

wherein R is an alkali metal, M is tantalum or columbium and X is fluorine or chlorine or bromine, and a diluent comprising an alkali metal halide at a temperature above the liquidus temperature of the salt mixture but not exceeding 760°C in a closed reaction vessel, adding a molten alkali metal to the bath at a rate of at least 0.2 kg per kg of the double salt per hour during a first period until a desired reaction temperature between 760°C and 1000°C is reached, the temperature rise during the first period being at a rate of at least 10K per minute, thereafter adding additional molten alkali metal to the bath at a rate of at least 0.1 kg per kg of the double salt per hour during a second period while providing forced cooling to the bath to extract heat at a rate of at least 42 kilojoules per minute per kilogram of the double salt, continuously agitating the liquid bath, continuously producing crystals of the metal M and collecting the crystals in a lower portion of the reaction vessel, the rate of alkali metal addition and the rate of forced cooling being adjusted to maintain the reaction temperature during the growth period within 50K of the desired reaction temperature but in excess of 760°C.

According to another aspect of the invention, a process for producing tantalum powder comprises maintaining a liquid bath of potassium fluotantalate and from about 0.6 to about 1.0 parts by weight of a diluent comprising sodium chloride at a temperature above the liquidus temperature of the salt mixture but not exceeding 660°C in a closed reaction vessel, adding molten sodium to the bath at a rate of at least 0.2 kg per kg of the potassium fluotantalate per hour during a first, nucleation period until a desired reaction temperature between 760°C is reached, the temperature rise during the first period being at a rate of at least 20K per minute, thereafter adding additional molten sodium to the bath at a rate of at least 0.1 kg per kg of the potassium fluotantalate per hour during a second, growth period while providing forced cooling to the bath by means of a high velocity air stream applied to the exterior of the vessel to extract heat at a rate of at least 42 kilojoules per minute per kilogram of the potassium fluotantalate, continuously agitating the liquid bath with an agitator maintained within the bath, continuously producing crystals of tantalum and collecting the crystals in a lower portion of the reaction vessel, the rate of alkali metal addition and the rate of forced cooling being adjusted to maintain the reaction temperature during the second period within 25K of the desired reaction temperature but in excess of 760°C.

According to yet another aspect of the invention a process for producing tantalum or columbium powder comprises reduction of a double salt using an alkali metal, the double salt being of the formula R_2MX_7 , where R is an alkali metal, M is tantalum or columbium and X is fluorine or chlorine or bromine, comprising maintaining a bath including the double salt and a diluent comprising an alkali metal halide, at a temperature above the melting point of the salt mixture, introducing the alkali metal in the liquid state to the bath during a first period in which the temperature of the bath is caused to rise to a desired reaction temperature, and continuing to add the molten alkali metal during a second period in which the temperature of the bath is maintained within about 50K of the desired reaction temperature by means of forced external cooling.

In the past, tantalum (Ta) and columbium (Cb) metal powders have been produced principally by the following general methods.

1. Electrolytic reduction of K_2TaF_7 or K_2CbF_7 in molten baths with various diluents comprising the chloride and fluoride salts of sodium and potassium. In this method the production rate is limited by the electrolysis parameters, i.e. current and voltage. The concentration gradients established in this system prevent high yields being obtained and production rates are relatively low. In all cases, the resulting tantalum powders are relatively coarse and dendritic, and produce anodes for electrolytic capacitors having very low capacitive charge. Considerable amounts of impurities are transferred to the product due to the galvanic corrosive activity on the reaction vessel components.

2. Exothermic reactions in a closed vessel wherein the K_2TaF_7 or K_2CbF_7 is mixed or placed in alternate layers with a reducing agent, both in the solid form. The enclosed charge is indirectly heated until the exothermic reaction is spontaneously initiated. This uncontrollable reaction produces powders having a wide range of particle sizes at intermediate yield efficiencies. In order for these materials to be usable in the manufacture of anodes for electrolytic capacitors, they must be classified extensively. These powders have larger surface areas per unit weight than electrolytic powders. In addition, these types of reactions create hazardous conditions.

3. Stirred liquid phase reactions, such as described in U.S. Patent No. 2,950,185. In this method the K_2TaF_7 is heated in a reaction vessel to a specific temperature above the melting point. Then molten sodium is added at a relatively slow, uniform feed rate corresponding to about 0.02 kg sodium per kg of K_2TaF_7 per hour to effect the reaction. This is carried out under essentially isothermal conditions with agitation of the

bath effected by an internal agitator. In this method, the resulting powder has a wide range of particle sizes and correspondingly a proportionally large range of surface areas. In order for these materials to be acceptable for the manufacture of anodes for electrolytic capacitors, they require extensive classification to obtain the desired particle size. The capacitive charge that can be obtained from anodes derived from these 5 powders is in the intermediate range. In addition, these materials have high volumetric densities which limit their use to anodes pressed to densities higher than about 6.0 gm/cm^3 .

4. Stirred liquid phase with diluent salts present, such as described in U.S. Patent No. 2,994,603. The stirred reaction was advanced because it made possible the use of lower bath temperatures through the addition of diluent salts such as NaCl and KCl to the K_2TaF_7 charge. The sodium feed rate, where given, is 10 about 0.25 kg Na per kg K_2TaF_7 per hour, and no external cooling is disclosed until after completion of the reaction. Typically, total reduction times of about 8 hours are necessary even when small charges are used. These process conditions result in agglomerates of finely divided material, a tendency to pick-up impurities, and an excessive proportion of fines.

5. Mulling of diluent salt and K_2TaF_7 in the solid form with liquid sodium below 150°C , (such as described 15 in U.S. Patent Nos. 3,829,310 and 3,992,192), followed by heating the charge to a temperature at which a spontaneous exothermic reaction is initiated. The exothermic reaction is either agitated, intermittently agitated, or not agitated, until a maximum reaction temperature in the range of about 950°C is attained. The reaction is maintained at that constant temperature for 1 to 8 hours by indirect heating means. Since this exothermic reaction is not controllable the characteristics of the product cannot readily be modified to 20 achieve the various desired particle sizes and ultimately the desirable electrical characteristics. These materials therefore require classification or sorting to remove fine and coarse particles from the finished product prior to their utilization in the manufacture of anodes for electrolytic capacitors.

The objects which the invention seeks to provide are:

1. To manufacture at a high yield, tantalum metal powders of specific fine size and consistent uniformity 25 for the manufacture of anodes used in high capacitive charge electrolytic capacitors.

2. To manufacture tantalum metal powders of various desired sizes for use in powder metallurgy at a high rate of production and a high yield.

3. To produce tantalum metal powders of high specific capacitance and low bulk densities which permit the manufacture of anodes for electrolytic capacitors at low pressed densities which ultimately results in 30 adequately low dissipation factor devices.

4. To produce tantalum metal powders of finer sizes in which effectively the entire product is usable in the manufacture of anodes for electrolytic capacitors by virtue of the similarity in performance of all particles in the size range of the produced material.

5. To produce tantalum metal powders of fine particle size having very high specific capacitance without 35 the need of classification for the removal of specific sizes (e.g. 0 to 3 microns) or for the concentration of other specific sizes.

6. To produce tantalum metal powders for use in electrolytic capacitors having good cohesion characteristics in anodes pressed at densities of 5.5 gm/cm^3 and lower without the necessity of using binders.

7. To produce tantalum metal powders of high specific capacitance with close control over the process of 40 nucleation and over the size of particles during the sodium metal reduction of tantalum fluoride salts by means of controlling high sodium metal injection rates and controlling the rate of forced cooling applied to the reaction vessel.

8. To produce tantalum metal powders of fine and relatively uniform particle size from a uniform molten 45 bath of K_2TaF_7 and a diluent salt at a temperature slightly above the melting point of the salt mixture.

9. To produce tantalum metal powders of coarse particle size from a molten bath of K_2TaF_7 and a diluent salt maintained at a temperature slightly above the melting point of the mixture and employing high rates of sodium metal injection, continuous agitation, and forced external cooling to control the process and so achieve the desired particle size.

10. To produce tantalum metal powders of metallurgical grade from a molten bath maintained at a 50 temperature slightly above the melting point of the mixture and employing high rates of sodium metal injection, continuous agitation and forced external cooling to control the process and so achieve the desired particle size at a high rate of production and a high yield.

The present invention will be described with reference to a specific reactor, however, it will be appreciated 55 that reactors of other types and sizes may be used.

The process of the invention is not limited to the methods of cooling described but may include other cooling means.

The process of the invention will be described in general terms with reference to production of tantalum metal powder from an alkali metal tantalum halide, however, the process is equally applicable to the 60 production of columbium powder of various specific sizes from halide salts of columbium in the liquid form in combination with diluents NaCl and KCl and reduced with a reducing alkali metal, also in the liquid form.

In the process of the invention other diluent systems than those described may be used, for example the fluorides, chlorides, bromides, and iodides of the alkali metals provided that they are in a homogeneous liquid phase with the salt to be reduced.

65 In the process of the invention other alkali metal reducing agents than those described may be used, for

example potassium, lithium, rubidium, and cesium, provided that they are in a liquid state at the point of their injection into the reaction vessel.

In general, the process of the present invention is applicable to the reduction of double salts of the formula R_2MX_7 , when R is an alkali metal, M is a metal of the group consisting of tantalum and columbium and X is a halogen of the group consisting of fluorine, chlorine and bromine, to produce the metal M in powder form.

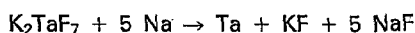
This period of the overall reaction, the said first period, during which the temperature of the charge increases from the initial bath temperature to the preferred reduction temperature is regarded herein as the "nucleation period" during which nucleation is controlled by the rate of sodium addition. When it is desired to produce very fine particle size tantalum powder metal to be used in the manufacture of anodes employed in the manufacture of high capacitive charge electrolytic capacitors, the sodium metal is preferably added at a very high rate until the reduction temperature is reached. To produce particles of an average size smaller than 5 microns (μm) it is preferred that the rate of temperature rise during the nucleation period be at least 20K per minute. For somewhat large particles (averaging 5 to 8 microns) the rate of temperature rise may be lower, but preferably at least 10K per minute. It has been found that the rate of sodium injection into the reactor during the nucleation period has an inverse effect on the particle size of the finished product. More specifically, it has been found that the average particle size of the finished product is inversely related to the rate of temperature rise during the nucleation period, and also to the time to complete the addition of the required stoichiometric amount of sodium at the desired reaction temperature during the second or "growth" period.

It has also been discovered that finer particle size tantalum powders may also be achieved by the use of large amounts of diluents such as NaCl, which also can serve as an internal heat absorber or heat sink in the system. Preferably, ratios of diluent to double salt in the range between about 0.6 and 1.0 (by weight) may be employed to produce smaller particles, averaging less than about 5 microns, while lower ratios from about 0.25 to about 0.6 (by weight) may be employed to produce somewhat larger particles, averaging from about 5 to about 8 microns.

It has also been discovered that fine particle sizes may be achieved by starting the sodium injection into the molten bath at the lowest possible temperature. Starting at a lower temperature may consume proportionally larger amounts of sodium for any given rate of temperature rise and consequently the overall process time may be reduced.

A further factor affecting particle size is the temperature of reduction. Temperatures from about 760°C to about 850°C tend to produce smaller particles, while temperatures from about 850°C to about 1000°C tend to produce somewhat larger particles.

Forced cooling may be used to maintain a controlled rapid temperature rise in the reaction mass at large sodium injection rates. This effects the extraction of a portion of the heat generated by the reaction.



The use of forced cooling may significantly reduce the overall process time and further reduce the particle size of the powder produced.

The term "forced cooling" as used herein refers to methods of temperature reduction apart from the natural cooling that takes place by heat loss through the walls of the reactor to ambient air and heat absorption that takes place as the relatively cool liquid alkali metal is heated up to bath temperature. These methods may comprise the use of high velocity streams of air or other coolant gas directed around the exterior of the reaction vessel, the use of a coolant jacket around the reaction vessel, the use of coolant coils within the reaction mass, or the use of coolant sprays of liquid directed against the exterior of the reaction vessel.

Preferably the rate of forced cooling will provide the removal of at least 42 kilojoules per minute per kilogram of the double salt and should represent at least 50% of the heat liberated by the reaction during the growth period. The rate of heat generation may be calculated from the rate of alkali metal feed and the heat of formation of the sodium fluoride product.

The rate of forced cooling may be calculated from the rate of coolant flow and the temperature rise of the coolant, taking into consideration its specific heat. Where the coolant changes phase, from liquid to vapour (as H_2O), or from solid to vapour (as CO_2), the latent heat of vaporization is also a factor.

Alternatively, the rate of forced cooling may be calculated (where the reaction temperature remains substantially constant) by subtracting from the rate of exothermic heat generation of a forced cooled system, the rate of exothermic heat generation of a similar system (maintained at the same temperature) which does not have forced cooling. In making the latter calculation, allowance should be made for the increased rate of heat absorption by reason of heating more alkali metal to bath temperature in the system utilizing forced cooling.

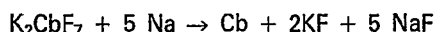
Thus by maintaining the rate of alkali metal feed during the growth period and the rate of forced cooling in balance the reaction temperature remains substantially constant during the growth period. The temperature should vary by no more than about 50K from the desired reaction temperature; preferably by no more than about 25K; and most preferably by no more than about 10K.

The combination of large amounts of diluent salt, low initial molten bath temperature, very fast sodium feed rate, and use of forced cooling to maintain a relatively constant temperature during the growth period

can result in a significantly more uniform and finer particle size powder than that obtainable from known processes.

The means described above for obtaining fine particle size tantalum metal powder with improved properties for the manufacture of anodes employed in the production of electrolytic capacitors can be equally well applied to the production of somewhat coarser particle size powders while still achieving the same added benefits of high productivity and high yield.

The improved process for the production of tantalum metal powders also can be applied to the production of other metal powders where controlled particle size is required at large productivity rates and high yields, such as columbium metal powder produced by the reaction



The invention may be performed in various ways, and some embodiments will now be described by way of example, with reference to the accompanying drawings, the Comparative and the Examples. In the drawings:

Figure 1 is a sectional view of apparatus suitable for carrying out the present invention;

Figure 2 is a graph of temperature against time for Examples 1, 2, 3 and 4.

Figure 3 is a graph of temperature against time for Examples 5 and 6.

Figure 4 is a comparison of the percentage of -80 Mesh powder produced in Examples 1, 2, 4 and 5.

Figure 5 is a comparison of the Fisher subsieve size of powders produced in Examples 1, 2, 4 and 5.

Figure 6 shows the specific capacitance of as-reduced, and (in some cases) thermally agglomerated, and phosphorus-doped powders produced in Examples 1, 2, 4 and 5 and pressed with a green density of 6.45 g/cm³ to 1.0-g anodes and sintered 30 minutes at 1600°C; and

Figure 7 is similar to Figure 6 but relates to a green density of 5.5 g/cm³.

In Figure 1 is shown a cross-section of a reactor vessel 50 for conducting reduction of K₂TaF₇ using rapid feed rates for the sodium reducing metal and forced external cooling. The vessel has thermal insulation 52 and can be heated by electrical resistance heating elements 54. Liner 56, constructed of a material such as stainless steel, surrounds a retort 58, which is constructed of a heat resistant alloy such as Inconel. Lid 59 of the retort has flange 60 sealed by gasket 62 to exterior port flange 100 of liner 56.

The molten salt bath 63 is comprised of a metal fluoride (or chloride) salt, such as K₂TaF₇, and a selected amount of diluent salt such as NaCl or KCl, or a mixture of these. The liquid level 63L of the salt bath and tantalum crystals 63C that build up during the reaction also are illustrated.

In the example embodiments of the invention to be described in greater detail, the salt bath is initially molten before the sodium addition. In the specific reactor used, the amount of K₂TaF₇ in the molten bath ranged from about 500 to 1000 kg and the diluent salt from about 200 to 450 kg, while the weight ratio of diluent salt to K₂TaF₇ ranged from about 0.2 to 1.0, and the mole ratios from about 0.8 to 4.6. The specific amounts of diluent salt and K₂TaF₇ used, and their weight ratio depends on the specific particle size of tantalum powder to be produced. The higher amounts of diluent salt were used when the finest particle size tantalum powders were produced.

When adequate volume was available in the retort, the entire amount of K₂TaF₇ and diluent salt were added as solid salts to the reactor and were melted together. In some cases where higher amounts of diluent salt were desired, all of the K₂TaF₇ and a portion of the diluent salt were melted first, then the balance of the diluent salt was added as one or more supplementary additions.

Agitation of the bath is maintained during the reduction reaction by agitator 64. The agitator has blades 66 with an outside diameter typically about one-half that of the inside diameter of the retort. The blades generally have a pitch in the range of about 30 to 60 degrees, typically about 45 degrees with respect to the agitator shaft.

The agitator extends vertically upward through seal 68 positioned on the retort lid to engage vertical drive means 70 and rotary drive means 72.

Agitation is provided continuously from the time the salt bath is molten until the completion of the reduction reaction. In preferred embodiments, the agitator speed is typically varied in the range from about 70 to 140 rpm during the run, or from about 0.05 to 0.50 rpm per kg of the molten salt mixture when said mixture is in the range of 500 to 1000 kg. The slower speeds are used initially to obtain a homogeneous molten salt bath before beginning the sodium feed. Fastest agitator speeds are used during the nucleation period when the highest sodium feed rate is used, then slower speeds are employed during subsequent lower sodium feed rates, and also after completion of the sodium feed.

Although changing agitator speeds during the run is a preferred procedure, satisfactory results can be achieved in this invention using a fixed agitator speed during the run.

Another preferred procedure is progressively to raise the position of the agitator during the period when the sodium is added. This is done using the vertical drive means to raise the agitator continuously or in steps, typically about 5 cms per step, upward about 10 to 30 cms above its initial position. This is done to avoid plowing of the tantalum metal powder particles that settle and progressively build up on the retort bottom, and to compensate for the added bath volume resulting from the sodium additions.

Although progressive raising of the agitator is a preferred practice, satisfactory results can be achieved in this invention by proper initial vertical placement of the agitator in an essentially mean position.

Specific combinations of agitator design, rotational speed and change, and intentional vertical raising of the agitator are used in an effort to achieve a continuously homogeneous bath composition during the runs made under diffi-different process conditions within the scope of this invention to achieve the desired final tantalum particle sizes.

5 Molten sodium at a temperature of about 100-160°C is introduced through line 74 extending through the retort lid. Drops or a stream 75 of sodium react in the molten bath when it contacts K_2TaF_7 as illustrated at 5
75R. The flow rate of sodium is controlled by valve 76 in the line from a heated sodium tank (not shown). Sodium condenser 80 is connected to the retort lid, and has a line 82 leading to a safety pop-off valve 84.
Thermocouple 86 is immersed in the molten bath and extends through seal 88 to a temperature recorder
10 and controller (not shown). 10

A means for forced external cooling of the retort is provided by blower 90. Ambient air or other coolant such as liquid or gaseous CO_2 are introduced at inlet 92 in the blower. The coolant flow proceeds through duct 94 connected to extension 96 leading to the interior of liner 56, then upward in the space 98 between the retort 58 and the liner to provide cooling to the retort. The coolant flow then proceeds through a collection
15 manifold 100 located at the top of the liner, then is vented through duct 102 containing a damper 104, or it 15
may be recirculated by providing a means for heat removal (not shown).

In the exemplary embodiments, forced air cooling on the exterior of the retort was generally used. With a 36-inch ID retort, air flow rates used to cool the exterior of the retort ranged from about 0.24 to 1.42 m^3/s . The highest rates were used in the process parameters employed to produce the finest tantalum powder particle
20 sizes. 20

Cooling of the retort can be further enhanced by providing fins or other suitable configurations on the exterior of the retort.

Forced air cooling and liquid carbon dioxide cooling are described in examples of the process. However such cooling methods are not limiting, and this invention also contemplates other means for forced cooling,
25 such as coolant coils or a coolant jacket, sprays, and other methods. 25

When this process is used for producing columbium by sodium reduction of K_2CbF_7 , the preferred ratio of diluent salt, such as NaCl, to K_2CbF_7 is about the same on a mole basis as for the ratio of NaCl to K_2TaF_7 , namely about 0.8 to 4.6 as described above. The preferred sodium feed rates for reducing K_2CbF_7 are about 30% greater than described in the examples for sodium reduction of K_2TaF_7 .
30 30

COMPARATIVE EXAMPLE 1

This describes a state-of-the-art practice for producing tantalum powder for use in electrolytic capacitor application. A stirred reaction with diluents was carried out using the reaction equipment illustrated in Figure 1, except that the reactor was not provided with a means for external forced cooling.

35 Quantities of 454.5 kg of K_2TaF_7 and 218 kg of NaCl were charged into a reaction vessel. The closed vessel 35
and its charge were heated to a temperature of 720°C. to melt the charge and the agitator was started soon thereafter to homogenize the liquid bath. Agitator speed was maintained at 70 rpm.

After a period of homogenization at 720°C, liquid sodium metal at a temperature of 148°C was added to the vessel at a rate of 0.301 kg/minute or 0.0397 kg of Na/kg of K_2TaF_7 per hour until a temperature of 790°C was
40 reached 120 minutes thereafter. Then an approximate liquid sodium metal injection rate of 0.211 kg of 40
Na/minute or 0.0279 g of Na/kg of K_2TaF_7 per hour was used to maintain a growth period temperature of 790°C. The growth period lasted 455 minutes or 7.55 hours; and during this period about 85.80 kJ/s were generated at the low sodium feed rate. During the growth period the agitator speed was continued to be maintained at 70 rpm.

45 The reaction mass was allowed to cool to ambient temperature and the tantalum metal powder produced 45
was recovered from the solidified mass by conventional state-of-the-art methods involving crushing and leaching.

Figure 2 is a graph of temperature vs time from the start to the end of the sodium metal feed. Note that in this graph the time cycle is shown in minutes up to one hour, and thereafter continues in hour intervals for
50 convenience in comparing this state-of-the-art example with embodiments of this invention described in the 50
later examples.

The tantalum powder was analyzed for chemical composition by conventional state-of-the-art procedures. The impurity levels that were determined are listed in Table I. The powder was subjected to a sieve analysis test using U.S. Standard screens to determine the percent by weight of +80 Mesh, -80 +325 Mesh, and
55 -325 Mesh material. The data are also listed in Table I, and the amount of -80 Mesh portions is plotted in 55
Figure 4. The -80 Mesh portions were combined, blended and used for all other tests.

The particle size of this powder was measured as Fisher sub-sieve size (FSSS) in accordance with ASTM designation B330-65, "Standard Method of Test for Average Particle Size of Refractory Metals and Compounds by the Fisher Sub-sieve Sizer". The data are included in Table I and plotted in Figure 4. Apparent
60 density, hereafter called "Scott density" (SD), was determined on this powder by the procedure of ASTM 60
designation B212-48, (Reapproved 1970), "Standard Method of Test for Apparent Density of Metal Powders", and the value is listed in Table I.

A portion of the -80 Mesh powder was tested for electrical properties in the "as-reduced" condition.

A second portion of the -80 Mesh powder was heated in a vacuum of about 10^{-3} torr absolute pressure to
65 about 1400°C (optical temperature), held for 1 hour at this temperature, cooled under vacuum for 2 hours and 65

finally under helium to ambient temperature, then milled and screened using a 35 Mesh screen, with any oversize material remilled and rescreened so that all powder was -35 Mesh. This tantalum powder is referred to as "thermally agglomerated" powder produced according to the teachings of U.S. (Pierret) Patent No. 3,473,915.

- 5 Each type of powder was individually weighed and pressed into 1.0 gram compacts or anodes with an embedded tantalum lead wire in a 0.54 cm diameter die to a green density of 6.45 g/cm³. Efforts to press compacts of these powders to a green density of 5.5 g/cm³ were unsuccessful because the green strengths were too low and inadequate for handling. 5
- The anodes pressed to a green density of 6.45 were sintered for 30 minutes at 1600°C (optical temperature) in a cold-wall, vacuum sintering furnace (10⁻⁵ torr absolute pressure). 10
- The percent shrinkage (in diameter) that occurred during sintering was determined. 10
- The electrical testing procedure involved anodizing the sintered anodes in 0.1% phosphoric acid in water at an electrolyte temperature of 90°C. Anodizing was carried out at a current density of 35 milliamps per gram until 100 volts was reached, and then they were held for 2 hours at 100 volts. The anodized anodes 15
- were washed in deionized water and then dried in clear air at 105°C. 15
- Direct current leakage (DCL) was measured at a test voltage of 70 volts in 10% phosphoric acid. The anodes were immersed in the test solution to the top of the anode and the test voltage was applied for 2 minutes, after which the DCL was measured.
- After DCL measurements were completed, the anodes were soaked in 10% phosphoric acid for 30 to 45 20
- minutes. 20
- The capacitance was measured on the anode immersed in 10% phosphoric acid employing a type 1611B General Radio Capacitance Test Bridge with an a.c. signal of 0.5 volts and a d.c. bias of 3 volts. The dissipation factor also was determined from this bridge test.
- The average values for shrinkage during sintering, DCL, specific capacitance (μfv/g), and dissipation factor 25
- for both the "as-reduced" and the "thermally agglomerated" powders are summarized in Table II. The specific capacitance data also are plotted in Figure 6. 25

EXAMPLE 2

- This example describes an embodiment of this invention using forced external air cooling on the reactor 30
- during a portion of the reduction cycle. 30
- A stirred reaction was carried out for the purpose of producing fine particle size tantalum powder having very high specific capacitance using a primary charge consisting of 454 kg of K₂TaF₇ and 218 kg of NaCl. The primary charge was heated in a closed reactor as described in Figure 1 and provided with a blower rated at 0.708 m³/s for applying forced external air cooling. The primary charge was heated to a temperature of 740°C 35
- to melt the charge, and the agitator was started soon thereafter to homogenize the primary liquid bath. After 35
- the primary liquid bath was homogenized, an additional 218 kg of NaCl at ambient temperature was introduced into the reaction vessel. The secondary charge was allowed to homogenize with the primary bath for approximately 15 minutes at which time a stable bath temperature of 640°C was reached. During the period of primary and secondary charge homogenization, an agitator speed of 120 rpm was employed. 40
- When the bath temperature reached a stable temperature of 640°C, liquid sodium metal at a temperature of 140°C was injected into the reaction vessel at a rate of 5.17 kg of Na/minute or 0.683 kg of Na/kg of K₂TaF₇ per hour until a charge temperature of 820°C was reached. This period of nucleation required 9 minutes. After reaching 820°C the blower providing the external forced cooling was turned on and maintained on during the balance of the growth period until the required amount of sodium metal had been added. During the growth 45
- period a sodium injection rate of 1.563 kg of Na/minute or 0.207 kg of Na/kg of K₂TaF₇ per hour was 45
- maintained in order to sustain a growth period temperature of 820°C ± 10 and to generate 632 kJ/s. The growth period covered 64 minutes or 1.06 hours. One hour after the start of sodium injection into the reactor the agitator speed was changed to 70 rpm and maintained at that speed until 1.5 hours after completion of the required sodium addition. A total of 135.6 kg of sodium was added to the reactor. During the growth 50
- period the forced air cooling extracted 525.3 kg/s or 1.088 kJ/s per kilogram of K₂TaF₇. 50
- The reaction mass was allowed to cool to ambient temperature and the tantalum metal powder produced was recovered as described in Example 1. To further illustrate this example, Figure 2 includes a graph of the temperature vs. time cycle from the start to the end of the sodium metal addition. Note that the total reduction time is only about one-sixth as long as that in Example 1.
- 55 The yield of -80 Mesh powder was 99.3% vs. 70% in Example 1, and the SD and FSSS of the powder from 55
- Example 2 also was substantially lower than the SD and FSSS of the powder from Example 1 as shown in Table I and Figures 4 and 5.
- A portion of the -80 Mesh powder was doped with 50 ppm contained phosphorus added by dryblending (NH₄)₂HPO₄ (diammonium phosphate) with the tantalum powder, then subjecting the powder to the above 60
- described thermal agglomeration treatment. This resulted in a "phosphorus-doped" tantalum powder 60
- according to the teachings of U.S. (Fry) Patent No. 4,009,007.
- The specific capacitance for anodes pressed at 6.45 g/cm³ and sintered 30 min. at 1600°C was about 42% higher than for anodes similarly pressed and sintered from the state-of-the-art powder of Example 1. The specific capacitance for anodes pressed at 5.5 g/cm³ was 11,160 μfv/g in the case of the phosphorus-doped 65
- powder. The test results are shown in Tables I, II and III and in Figures 4, 5, 6 and 7. 65

EXAMPLE 3

This example describes an embodiment of this invention for producing a tantalum powder of moderately coarse particle size.

- A stirred reaction was carried out for the purpose of producing a coarse particle size tantalum powder for powder metallurgy purposes using a primary charge consisting of 500 kg of K_2TaF_7 and 136 kg of NaCl. The primary charge was heated in a closed reactor as described in Figure 1 and provided with a blower rated at 0.708 m^3/s for applying forced external air cooling. The primary charge was heated to a temperature of 720°C to melt the charge, and the agitator was started soon thereafter to homogenize the primary liquid bath. During the period of primary homogenization an agitator speed of 100 rpm was employed.
- When the bath temperature reached a stable temperature of 720°C, liquid sodium metal at a temperature of 140°C was injected into the reaction vessel at a rate of 4.42 kg of Na/minute or 0.530 kg of Na/kg of K_2TaF_7 per hour until a charge temperature of 965°C was reached. This period of nucleation required 13 minutes. After reaching 965°C, the blower providing the external forced cooling was turned on and maintained on during the balance of the growth period or until the required amount of sodium metal had been added.
- During the growth period a sodium injection rate of 1.38 kg of Na/minute or 0.166 kg of Na/kg of K_2TaF_7 per hour was maintained in order to sustain a growth period temperature of 965°C \pm 25K. The 98.4 kg growth period consumed 67 minutes or 1.1 hours. During the period of injection into the reactor, the agitator speed was maintained at 120 rpm until 1.5 hours after completion of the required sodium addition. A total of 148.5 kg of sodium was added to the reactor. During the growth period, the reaction generated 554.6 kJ/s and the forced cooling extracted 446.5 kJ/s, or 0.8943 kJ/s kilogram of K_2TaF_7 .
- The reaction mass was allowed to cool to ambient temperature and the tantalum metal powder produced was recovered as described in Example 1. Figure 2 includes a graph showing the temperature vs. time cycle from the start to the end of sodium metal addition. The total reduction time was only about one-sixth that of Example 1.
- The values for chemical composition, sieve analysis, SD and FSSS are listed in Table I, and are generally similar to those for Example 1.

EXAMPLE 4

- In this example an embodiment is described for producing a fine particle size tantalum powder in which liquid CO_2 was employed in forced external cooling of the retort.
- A stirred reaction was carried out for the purpose of producing fine particle size tantalum powder having very high specific capacitance using a primary charge consisting of 454 kg of K_2TaF_7 and 218 kg of NaCl. The primary charge was heated in a closed reactor as described in Figure 1, and provided with a blower rated at 0.708 m^3/s for applying forced external cooling. In addition, means to introduce liquid CO_2 into the entrance port of the blower was provided. The primary charge was heated to a temperature of 730°C to melt the charge, and the agitator was started soon thereafter to homogenize the primary liquid bath. After the primary liquid bath was homogenized, an additional 218 kg of NaCl at ambient temperature was introduced into the reaction vessel. The secondary charge was allowed to homogenize with the primary bath for approximately 15 minutes at which time a stable bath temperature of 640°C was reached. During the period of primary and secondary charge homogenization, an agitator speed of 120 rpm was employed.
- When the bath temperature reached a stable temperature of 640°C, liquid sodium metal at a temperature of 140°C was injected into the reaction vessel at a rate of 6.32 kg of Na/minute or 0.835 kg of Na/kg of K_2TaF_7 per hour until a charge temperature of 800°C was reached. This period of nucleation required 8 minutes. After reaching 800°C the blower providing the external forced cooling was turned on and maintained on during the balance of the growth period or until the required amount of sodium metal had been added. In addition, simultaneously with the introduction of the forced air external coolant, liquid CO_2 was introduced in the sublimed form into the suction port of the blower. The CO_2 additional cooling was maintained for approximately 10 minutes, wherein approximately 54.5 kg of CO_2 were consumed. During the growth period, a sodium injection rate of 2.18 kg of Na/minute or 0.288 kg of Na/kg of K_2TaF_7 per hour was used in order to maintain a growth period temperature of 800°C \pm 10K. The growth period consumed 50 minutes or 0.83 hours. One hour after the start of sodium injection into the reactor, the agitator speed was changed to 70 rpm and maintained at that speed until 1.5 hours after completion of the required sodium addition. A total of 135.6 kg of sodium were added to the reactor. During the growth period, the reaction generated 929.2 kJ/s, the forced air and carbon dioxide cooling extracted an average of 813.4 kJ/s or 1.791 kJ/s per kilogram of K_2TaF_7 .
- The reaction mass was allowed to cool to ambient temperature and the tantalum metal powder produced was recovered as described in Example 1. Figure 2 includes a graph showing the temperature vs. time cycle from the start to the end of sodium metal addition. The total reduction time was less than one-eighth that of Example 1.
- Compared to the state-of-the-art powder from Example 1, the powder produced by the process of Example 4 showed a much higher amount of -80 Mesh material, lower SD and FSSS, and a specific capacitance about 58% higher for as-reduced powder pressed at 6.45 g/cm^3 and sintered 30 minutes at 1600°C. The specific capacitance for as-reduced and for thermally agglomerated powders pressed at 5.5 g/cm^3 and sintered for 30 minutes at 1600°C also was higher than for the embodiments described in Example 2. The test results are shown in Tables I, II and III and in Figures 4, 5, 6 and 7.

EXAMPLE 5

In this example an embodiment of the invention is described for producing a fine particle size tantalum powder in which external forced air cooling was employed during the entire time when sodium was fed.

A stirred reaction was carried out for the purpose of producing fine particle size tantalum powder having very high specific capacitance using a primary charge consisting of 454 kg of K_2TaF_7 and 218 kg of NaCl. The primary charge was heated in a closed reactor as described in Figure 1 and provided with a blower rated at 0.708 m^3/s for applying forced external air cooling. The primary charge was heated to a temperature of 740°C to melt the charge, and the agitator was started soon thereafter to homogenize the primary liquid bath. After the primary liquid bath was homogenized, an additional 218 kg of NaCl at ambient temperature was introduced into the reaction vessel. The secondary charge was allowed to homogenize with the primary bath for approximately 15 minutes at which time a stable bath temperature of 640°C was reached. During the period of primary and secondary charge homogenization, an agitator speed of 120 rpm was employed.

When the bath temperature reached a stable temperature of 640°C, liquid sodium metal at a temperature of 140°C was injected into the reaction vessel at a rate of 6.72 kg of Na/minute or 0.888 kg of Na/kg of K_2TaF_7 per hour until a charge temperature of 800°C was reached. This rate is about 22 times as fast as that used in Example 1. This period of nucleation required 8 minutes. Simultaneously with the start of sodium metal injection the blower that provided the forced air external cooling was turned on and maintained on during both the entire nucleation period and growth periods until the completion of the sodium metal addition. During the growth period, a sodium injection rate of 2.14 kg of Na/minute or 0.283 kg of Na/kg of K_2TaF_7 per hour was maintained in order to maintain a growth period temperature of 800°C \pm 10K. This rate is more than 10 times as fast as that used in Example 1. The growth period consumed 50 minutes or 0.83 hours. One hour after the start of sodium injection into the reactor the agitator speed was changed to 70 rpm and maintained at that speed until 1.5 hours after completion of the required sodium addition. A total of 135.6 kg of sodium was added to the reactor. During the growth period, the reaction generated 929.88 kJ/s; the forced air cooling extracted 813.38 kJ/s, or 1.794 kJ/s per kilogram of K_2TaF_7 .

The test results are shown in Tables I, II and III and in Figures 4, 5, 6 and 7.

The reaction mass was allowed to cool to ambient temperature and the tantalum metal powder produced was recovered as described in Example 1. Figure 3 includes a graph showing the temperature vs. time cycle from the start to the end of sodium metal addition.

Compared to Example 1, the powder produced by the process of Example 5 exhibited a much higher % - 80 Mesh material, much lower SD and FSSS, and about 58% higher specific capacitance (as-reduced powder pressed at 6.45 g/cm^3 , sintered 30 minutes at 1600°C.)

EXAMPLE 6

This example, like Example 3, describes an embodiment of the invention for producing a coarse particle size tantalum powder, but using still faster sodium feed rates and a larger charge of K_2TaF_7 and diluent salt.

A stirred reaction was carried out for the purpose of producing coarse particle size tantalum powder for powder metallurgy purposes using a primary charge consisting of 636 kg of K_2TaF_7 and 173 kg of NaCl. The primary charge was heated in a closed reactor as described in Figure 1 and provided with a blower rated at 0.708 m^3/s for applying forced external air cooling. The primary charge was heated to a temperature of 750°C to melt the charge, and the agitator was started soon thereafter to homogenize the primary liquid bath. During the period of primary charge homogenization an agitator speed of 120 rpm was employed.

When the bath temperature reached a stable temperature of 750°C, liquid sodium metal at a temperature of 140°C was injected into the reaction vessel at a rate of 6.20 kg of Na/minute or 0.583 kg of Na/kg of K_2TaF_7 per hour until a charge temperature of 985°C was reached. This period of nucleation required 6 minutes. After reaching 985°C, the blower providing the external forced cooling was turned on and maintained on during the balance of the growth period or until the required amount of sodium metal had been added. During the growth period a sodium injection rate of 1.58 kg of Na/minute or 0.149 kg of Na/kg of K_2TaF_7 per hour was maintained in order to maintain a growth period temperature of 985°C \pm 25K. The growth period consumed 103 minutes or 1.71 hours. During the period of nucleation and growth the agitator speed was 120 rpm and was maintained at that speed until one hour after completion of the required sodium addition. The total of 189.9 kg of sodium was added to the reactor. During the growth period, the reaction generated 635.5 kJ/s and the forced cooling extracted 528.8 kJ/s or 0.8322 kJ/s per kilogram of K_2TaF_7 .

The reaction mass was allowed to cool to ambient temperature and the tantalum metal powder produced was recovered as described in Example 1. Figure 3 includes a graph showing the temperature vs. time cycle from the start to the end of sodium metal addition.

The as-reduced powder had a FSSS of 5.85 microns and a SD of 68.2 g/cm^3 .

The physical properties and the chemical compositions of the powders produced in Examples 1 to 6 are shown in Table I.

TABLE 1
PHYSICAL PROPERTIES AND CHEMICAL
COMPOSITIONS OF AS-REDUCED POWDERS

5 Example No.		1	2	3	4	5	6	5	
<i>Sieve Analysis, %</i>									
	+80 Mesh	30.0	0.7	21.0	2.9	1.1	-		
10	-80 + 325 Mesh	35.0	20.9	4.1	28.9	24.6	-	10	
	-325 Mesh	35.0	78.4	74.9	68.2	74.3	-		
<i>Fisher Sub sieve Size, μm</i>									
15	(-80 Mesh)	7.10	2.30	7.20	2.60	2.70	5.85	15	
<i>Scott Density, g/in^3 (-80 Mesh)</i>									
		52.4	36.5	62.4	41.3	36.3	68.2		
<i>20 Chemical Composition</i>									
		<i>ppm</i>							20
	O ₂	809	1366	850	2159	1397	-		
	C	<10	12	-	43	18	-		
25	N	20	18	-	32	53	99	25	
	Fe	29	100	20	68	36	40		
	Cr	<10	24	15	22	18	15		
	Ni	<10	38	20	48	18	55		
	Cb	<10	<10	<10	<10	<10	<10		
30	Si	<10	35	<10	17	40	-	30	
	Ca	<10	<10	<10	14	<10	-		
	W	<50	-	<50	-	-	<50		
	Na	<10	-	-	-	-	-		

35 The data obtained from the tests run on anodes made from the powders of Examples 1, 2, 4 and 5 when the powders were pressed to a green density of 6.45 g/cm^3 are shown in Table II: 35

TABLE II

ELECTRICAL CHARACTERISTICS OF SINTERED 1.0 GRAM ANODES OF AS-REDUCED, THERMALLY AGGLOMERATED, AND PHOSPHORUS-DOPED CAPACITOR POWDERS PRESSED TO GREEN DENSITY OF 6.45 g/cm³ (ANODES SINTERED FOR 30 MIN. AT 1600°C)

Example No.	1	2	4	5
<i>As-Reduced Powder</i>				
Capacitance, μfv/g	5393	7656	8538	8537
DCL, μa/g	3.8	2.5	2.7	3.9
Dissipation Factor, %	34	70	-	58
Shrinkage During Sintering, %	1.2	9.3	7.4	4.1
<i>Thermally Agglomerated Powder</i> (Agglomerated 1 hr. at 1400°C.)				
Capacitance, μfv/g	5976	7428	8954	-
DCL, μa/g	2.0	1.4	12.5	-
Dissipation Factor, %	36	38	40	-
Shrinkage During Sintering, %	1.6	7.4	4.9	-
<i>Phosphorus-Doped Powder</i> (Doped with 50 ppm P added as (NH ₄) ₂ HPO ₄ , thermally agglomerated 1 hr. at 1400°C.)				
Capacitance, μfv/g	-	10,194	10,554	-
DCL, μa/g	-	3.0	17.5	-
Dissipation Factor, %	-	39	43	-
Shrinkage During Sintering, %	-	4.7	3.1	-

The data obtained from the test run on anodes made, or attempted to be made, from the powders of Examples 1, 2, 4 and 5 when the powders were pressed, or attempted to be pressed, to a green density of 5.5 g/cm³ are shown in Table III:

TABLE III

ELECTRICAL CHARACTERISTICS OF SINTERED 1.0 GRAM ANODES OF AS-REDUCED, THERMALLY AGGLOMERATED, AND PHOSPHORUS-DOPED CAPACITOR POWDERS PRESSED TO GREEN DENSITY OF 5.5 g/cm³ (ANODES SINTERED FOR 30 MIN. AT 1600°C.)

Example No.	1	2	4	5
<i>As-Reduced Powder</i>				
Capacitance, μfv/g	-	8901	9495	-
DCL, μa/g	-	3.0	3.1	-
Dissipation Factor, %	-	56	-	-
Shrinkage During Sintering, %	-	10.1	8.1	-
<i>Thermally Agglomerated Powder</i> (Agglomerated 1 hr. at 1400°C)				
Capacitance, μfv/g	-	8348	8428	7557
DCL, μa/g	-	1.3	1.6	1.6
Dissipation Factor, %	-	29	28	27
Shrinkage During Sintering, %	-	9.4	8.2	3.2
<i>Phosphorus-Doped Powder</i> (Doped with 50 ppm P added as (NH ₄) ₂ HPO ₄ , thermally agglomerated 1 hr. at 1400°C.)				
Capacitance, μfv/g	-	11,160	10,155	10,158
DCL, μa/g	-	3.8	5.1	4.0
Dissipation Factor, %	-	34	33	35
Shrinkage During Sintering, %	-	4.2	5.6	3.8

- Could not press; green strength too low -

CLAIMS

1. A process for producing tantalum or columbium powders which comprises maintaining a liquid bath of a double salt of the formula
- $$R_2MX_7$$
- wherein R is an alkali metal, M is tantalum or columbium and X is fluorine or chlorine or bromine, and a diluent comprising an alkali metal halide at a temperature above the liquidus temperature of the salt mixture but not exceeding 760°C in a closed reaction vessel, adding a molten alkali metal to the bath at a rate of at least 0.2 kg per kg of the double salt per hour during a first period until a desired reaction temperature between 760°C and 1000°C is reached, the temperature rise during the first period being at a rate of at least 10K per minute, thereafter adding additional molten alkali metal to the bath at a rate of at least 0.1 kg of the double salt per hour during a second period while providing forced cooling to the bath to extract heat at a rate of at least 42 kilojoules per minute per kilogram of the double salt, continuously agitating the liquid bath, continuously producing crystals of the metal M and collecting the crystals in a lower portion of the reaction vessel, the rate of alkali metal addition and the rate of forced cooling being adjusted to maintain the reaction temperature during the growth period within 50K of the desired reaction temperature but in excess of 760°C.
2. A process as claimed in Claim 1 in which the salt is K_2TaF_7 , the molten alkali metal is sodium and the diluent is selected from the group consisting of NaCl, KCl and mixtures thereof.
3. A process as claimed in Claim 1 or Claim 2 in which the cooling includes a high velocity air stream applied to the exterior of the reaction vessel.
4. A process as claimed in Claim 3 in which the forced cooling is applied throughout the periods of sodium addition.
5. A process as claimed in any of Claims 2 to 4 in which the salt is NaCl and is present in the liquid bath in a weight ratio from about 0.25 to about 1.0 with respect to the K_2TaF_7 .
6. A process as claimed in Claim 5 in which the weight ratio is from about 0.6 to about 1.0 and the process produces a tantalum metal powder having an average particle size of less than about 5 microns, measured by the Fisher Sub-Sieve Sizer.
7. A process as claimed in Claim 5 in which the ratio is from about 0.25 to about 0.60 and the process produces a tantalum powder having an average particle size of between about 5 and about 8 microns, measured by the Fisher Sub-Sieve Sizer.
8. A process as claimed in any of Claims 2 to 5 in which of the weight of the tantalum crystals is -325 Mesh.
9. A process as claimed in any of the preceding Claims in which the salt bath is maintained at a temperature not exceeding 660°C before the start of alkali metal addition.
10. A process as claimed in any preceding Claim in which during the second period is maintained within 25K of the desired reaction temperature.
11. A process as claimed in Claim 10 in which during the second period is maintained within 10K of the desired reaction temperature.
12. A process claimed in any of Claims 2 to 11 in which during the second period is maintained between about 760°C and about 850°C and the tantalum crystals average from about 5 microns in size by Fisher Sub-Sieve Sizer.
13. A process as claimed in any of Claims 2 to 10 in which during the second period is maintained between about 850°C and about 1000°C and the tantalum crystals average less than about 5 to about 8 microns in size by Fisher Sub-Sieve Sizer.
14. A process as claimed in any preceding Claims in which the agitation is provided by an agitator maintained above the level of the formed tantalum or columbium metal crystals that collect in the reaction vessel and below the liquid level of the bath by raising the level of the agitator during the periods of alkali metal additions.
15. A process in which the agitator is provided by an agitator having a shaft and having blades which measure about one-half the diameter of the reaction vessel, the blades having a pitch of between 30° and 60° with respect to the agitator shaft, and the agitator rotates at a speed within the range 0.05 to 0.50 rpm per kg of the salt mixture when the total weight of the mixture is between 500 and 1000 kg.
16. A process as claimed in Claim 15 in which the agitator rotational speed is varied within the said range at least once during the reaction cycle.
17. A process for producing tantalum powder which comprises maintaining a liquid bath of potassium fluotantalate and from about 0.6 to about 1.0 parts by weight of a diluent comprising sodium chloride at a temperature above the liquidus temperature of the salt mixture but not exceeding 660° in a closed reaction vessel, adding molten sodium to the bath at a rate of at least 0.2 kg per kg of the potassium fluotantalate per hour during a first nucleation period until a desired reaction temperature between 760°C and 850°C is reached, the temperature rise during the first period being at a rate of at least 20k per minute, thereafter adding additional molten sodium to the bath at a rate of at least 0.1 kg per kg of the potassium fluotantalate per hour during a second growth period while providing forced cooling to the bath by means of a high velocity air steam applied to the exterior of the vessel to extract heat at a rate of at least 42 kilojoules per

minute per kilogram of the potassium fluotantalate, continuously agitating the liquid bath with an agitator maintained within the bath, continuously producing crystals of tantalum and collecting the crystals in a lower portion of the reaction vessel, the rate of alkali metal addition and the rate of forced cooling being adjustable to maintain the reaction temperature during the second period within 25K of the desired reaction temperature but in excess of 760°C.

18. A process as claimed in Claim 17 in which the forced cooling includes a high velocity stream of carbon dioxide applied to the exterior of the vessel.

19. A process for producing tantalum substantially as herein specifically described with reference to any one of Examples 2 to 6, and with reference to the accompanying drawings.

20. A process for producing tantalum or columbium powder by the reduction of a double salt using an alkali metal, the double salt being of the formula R_2MX_7 , where R is an alkali metal M is tantalum or columbium and X is fluorine or chloride or bromine, comprising maintaining a bath including the double salt and a diluent comprising an alkali metal halide, at a temperature above the melting point of the salt mixture, introducing the alkali metal in the liquid state to the bath during a period in which the temperature of the bath is caused to rise to a desired reaction temperature, and continuing to add the molten alkali metal during a second period in which the temperature of the bath is maintained within about 50K of the described reaction temperature by means of forced external cooling.

21. Tantalum or columbium powders which have been produced by the method of any of the preceding claims.