July 27, 1948. H. C. RENTSCHLER ET AL 2,446,062

MANUFACTURE OF THORIUM

Filed Jan. 23, 1945 2 Sheets-Sheet 1

Fig. 1.

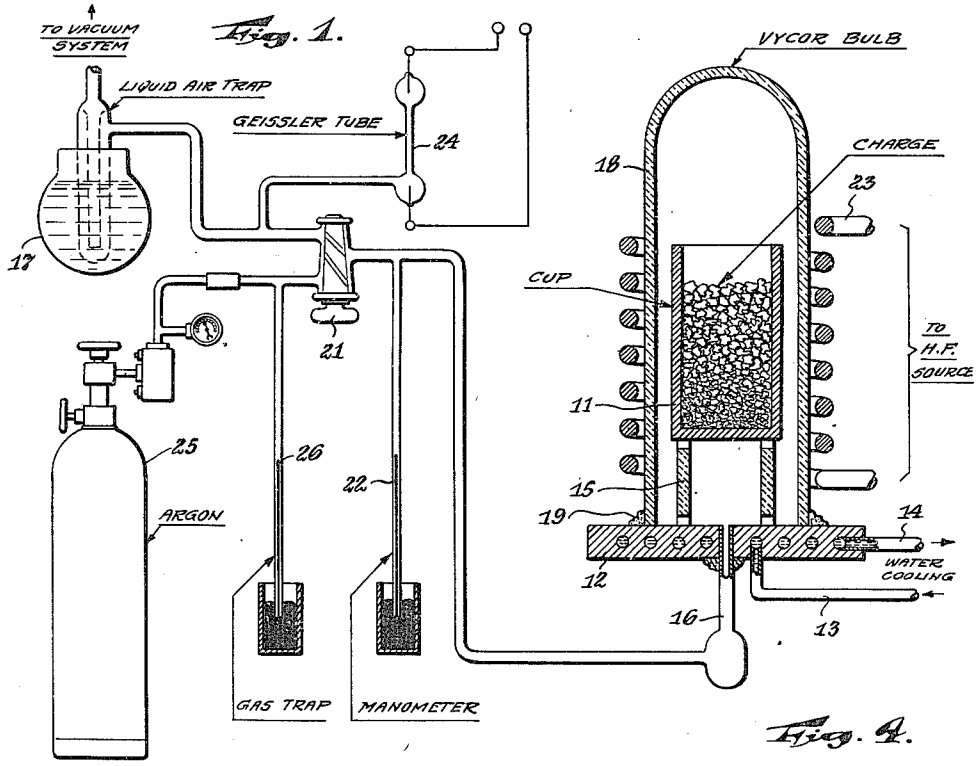


Fig. 4.

Fig. 2.

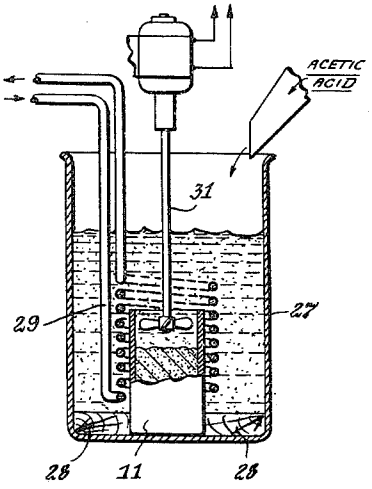
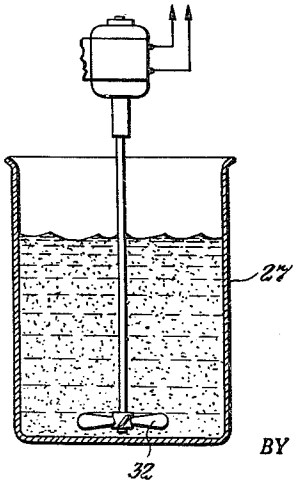
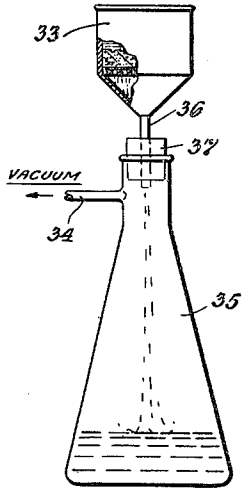


Fig. 3.





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Fig. 5.

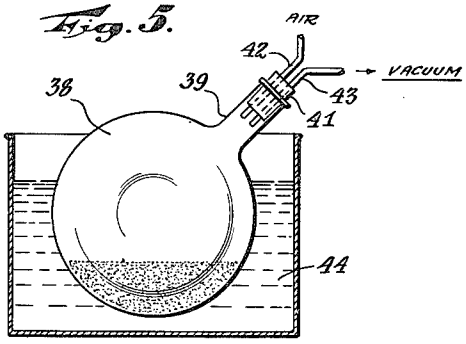


Fig. 6.

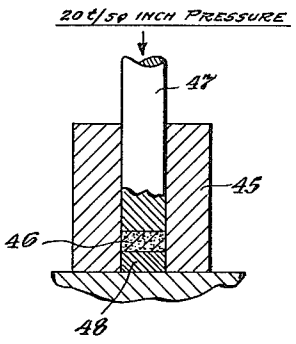
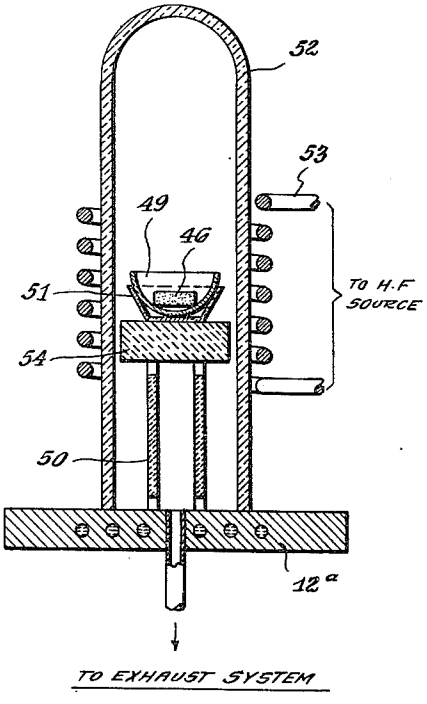


Fig. 8.

Fig. 7.



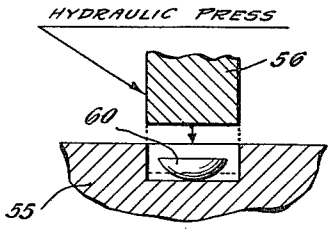


Fig. 9.

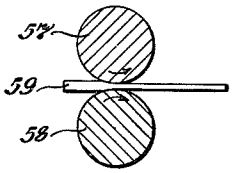
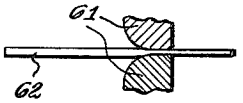


Fig. 10.



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UNITED STATES PATENT OFFICE

2,446,062

MANUFACTURE OF THORIUM

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Application January 23, 1945, Serial No. 574,130

9 Claims. (Cl. 75—84)

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This invention relates to thorium, more particularly to the production of metal of an exceptionally high degree of purity, and to an improved method for the manufacture thereof.

The principal object of our invention, generally considered, is to produce thorium by reaction of the oxide with calcium, said reaction taking place in an open cup enclosed in a container, said container being filled with an inert gas, as distinguished from the prior practice of reducing the oxide in a heavy-walled iron bomb with a ground-in stopper, said bomb being heated in open air.

Another object of our invention is to produce thorium powder by heating the oxide and calcium by high-frequency induction, the reaction cup being enclosed in a high-silica glass bell jar, such as one of 96% silica glass.

A further object of our invention is to treat the powder produced in accordance with the above, to consolidate it into coherent metal and to form to the desired shape.

Other objects and advantages of the invention will become apparent as the description proceeds.

Referring to the drawing:

Fig. 1 is a diagrammatic view, with parts in section, of apparatus for producing thorium in powder form.

Fig. 2 is a vertical sectional view of apparatus for leaching the contents of the cup used in the reduction of thorium oxide, to remove the thorium produced therein.

Fig. 3 is a vertical sectional view of apparatus for washing the thorium powder produced.

Fig. 4 is an elevational view of apparatus, with parts in vertical section, illustrating how the powder produced may be washed and dried.

Fig. 5 is a vertical sectional view, with parts in elevation, of apparatus for completing the drying of the thorium powder.

Fig. 6 is a vertical sectional view, with a part in elevation, of apparatus for producing slugs from thorium powder.

Fig. 7 is a vertical sectional view of apparatus for melting a slug of thorium, such as produced by apparatus shown in preceding figures.

Fig. 8 is a vertical sectional view of a hydraulic press which may be employed for reshaping the pellets of thorium produced by melting, prior to final forming.

Fig. 9 is a vertical sectional view of rolls which may be employed for forming the produced thorium into sheet.

Fig. 10 is a vertical sectional view of a die

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which may be used for drawing thorium into wire.

The reduction of rare metal oxides, including thoria, by calcium or other reducing agents, has previously been accomplished in heavy-walled iron bombs, with a ground-in stopper held in place by a screw cap. Such devices have a number of limitations and disadvantages, to wit:

It is difficult to maintain an air-tight joint between the stopper and bomb and to prevent reoxidation of the thorium powder produced as the bomb cools, or during the heating process. Considerable warping of the bomb occurs during heating and cooling, thus necessitating time-consuming lapping operations between runs. The construction of bombs has been limited to materials which will resist oxidation at elevated temperatures, and iron or iron alloys have been generally used for economy. Bombs were without exception of heavy-walled construction to permit sufficient surface area for sealing and presumably to withstand pressure produced in the reaction.

From thermo-chemical data and a consideration of the products formed in the reaction between thorium oxide and calcium, we concluded that the pressures developed in the reaction were insufficient to necessitate the heavy-walled bombs previously used. We tested our conclusions by placing an open iron cup under a high-silica glass bell jar, evacuating the bell jar, and then heating the iron cup by high frequency induction to cause the calcium to reduce the thorium oxide. Vaporization of the calcium was suppressed by filling the jar with argon gas at a pressure slightly less than atmospheric. There was no abnormal pressure produced during the reaction, very little vaporization of calcium, and satisfactory thorium metal was obtained.

The invention to be disclosed, therefore, differs from prior practice in the following respects and obviates several limitations of former practice. The heating, reaction, and cooling of the charge is carried out under known, controlled, and reproducible conditions of gas filling and exhaust. The reaction is carried out in an open vessel or cup of relatively thin wall. Oxidation of the cup and thorium produced is entirely prevented by working in an atmosphere free of oxygen. A choice of several materials of construction for the cup may be made, the only limitation being the melting point and chemical activity of the material with thorium and calcium at elevated temperatures. Thus the cup may be made out of a metal of high melting point,

such as molybdenum, which permits the reduction to be made at temperatures at least up to 1400° C. or higher. The use of such temperatures results in an increase in the fluidity of the charge and a faster and more complete reduction.

In Fig. 1 there is shown apparatus for effecting the reduction of thorium oxide to metal. This involves a cup or crucible **11** formed of a suitable metal, relatively inert to the charge and thorium at elevated temperatures, preferably molybdenum, although a molybdenum-lined iron cup, or one formed of iron or steel may be employed. However, if thorium of a very low iron content is desired, molybdenum or its equivalent must be used. The cup is supported above a metal plate **12** which is preferably cooled by circulating water therethrough by means of inlet pipe **13** and outlet pipe **14**. The cup preferably rests on a hollow refractory insulator **15**. A mixture of thorium oxide and granulated, distilled calcium (5 to 10 mesh) is placed in the cup. The preferred mixture is 400 gms. of thorium oxide and 240 gms. of calcium, which represents an excess of approximately 98% or 100% over that theoretically required, in accordance with the equation:

$$ThO_2+2Ca \rightarrow Th+2CaO$$

This proportion is preferred, although satisfactory metal has been produced with as low as 75% excess of calcium. As previously mentioned, it is desirable to produce as fluid a condition of the charge as possible during the reduction, and increasing the excess of calcium promotes this condition.

The metal plate **12** is tubulated, as indicated at **16**, and connected to a high vacuum exhaust system which may conveniently be comprised of a high vacuum pump, or mercury diffusion pump, and a liquid air trap **17**. A 96% silica bell jar **18**, just large enough to slip over the cup, is set on the metal base and sealed vacuumtight, preferably by means of vacuum wax **19**, to provide a gas-tight enclosure. The jar is then exhausted to a high vacuum through valve or stop cock **21**, a Geissler tube **24** serving to indicate the degree of exhaust obtained.

A high frequency coil **23** is then placed around the bell jar **18** and the cup slowly heated by induction to approximately 700° C., without substantially heating the enclosure and thereby maintaining the gas-tight condition, pumping out any gas evolved and continuing this operation until the degree of exhaust is below that supporting a discharge in the Geissler tube **24**. Argon gas (99.7%) is then introduced, as from tank **25** through valve **21** to a pressure of about two-thirds to one atmosphere. A mercury column **22** indicates this pressure. A gas trap or "blow-off" **26**, comprising a mercury column, is also provided. The metal cup **11** is then slowly heated by energizing the coil **23** to melt the calcium and reduce the thorium oxide to metal powder.

Under the conditions specified, the reaction appears to start at a temperature of approximately 800° C. to 900° C., noted by the appearance of a fine white mist, which is calcium vapor. When this is observed, the temperature is raised to approximately 1400° C. and the cup held at this temperature for a period of about ten minutes. This moderate period of heating has been found to be sufficient for a satisfactory reduction at the temperature stated.

After the cup and charge have thoroughly cooled, the cup is removed and placed in a jar or receptacle **27** containing water and acetic acid, which dissolves the excess calcium and the calcium oxide formed in the reaction, as represented in Fig. 2. While in the receptacle **27**, the cup **11** is preferably centered, as by means of a block of wood **28**, and cooled during the process of leaching as by means of a coil of pipe **29**, preferably stainless steel, through which water circulates. The mixture of water and acetic acid is preferably stirred as by means of a stainless steel motor-driven stirrer **31**.

A desirable manner of leaching is to add 6 to 8 liters of water to the jar **27** of 10 to 12 liters' capacity. Acetic acid is added gradually, 100 to 200 cc. at a time, until approximately one liter has been added, stirring continuously to complete removal of the charge from the cup. This operation usually takes from 3 to 8 hours, depending upon local conditions of heating during reduction.

After the charge is leached out of the cup, the wooden block, molybdenum cup, and cooling coil, are removed, and the powder allowed to settle for about 20 minutes. The supernatant liquid is poured off and about 3 liters of water added, plus an equal volume of glacial acetic acid, and stirring is continued for about 1 hour with the propeller **32** of the stirring apparatus well down into the jar to insure maximum agitation, as represented in Fig. 3. The powder is then allowed to settle for about 15 minutes and the supernatant liquid poured off.

The powder in the bottom of the container is then washed with water, using 4 to 5 liters per wash, stirring for 5 minutes, and settling for 15 minutes between pouroffs. This operation is repeated 9 or 10 times.

During the first washings, the supernatant liquid is cloudy due to the presence of fines. These are not filterable and are discarded. As the supernatant liquid becomes clearer, a white turbidity appears which is probably due to the reaction of the acid and water on very fine particles. With continued washing, this cloudiness disappears, and when this point is reached the powder is thrown on Büchner funnel **33**, as illustrated in Fig. 4, using suction as applied to tube **34** of flask **35**. A relatively coarse filter paper is preferably used in the funnel, the tubulation **36** of which passes through a cork **37** in the neck of flask **35**. The powder is washed with water until the filtrate is clear, and then with alcohol and ether in succession.

The metal powder, after removal from the Büchner funnel, is dried in a spherical flask **38** having a neck **39** receiving a cork **41** through which tubes **42** and **43** pass, one of said tubes being connected to a vacuum pump as illustrated in Fig. 5. Such an arrangement permits the powder to be dried under vacuum conditions. The complete removal of moisture is obtained by immersing the flask with the vacuum on in water **44** at 60° C. to 70° C. and shaking the flask intermittently until such removal is noted by the absence of dusting upon shaking.

Thorium powder, such as produced in accordance with the aforedescribed method, may be worked as by first pressing into pellets and heat treating in vacuo at 1200° C. to 1400° C. After such treatment the metal may be cold deformed by the usual operations such as rolling, swaging, or drawing. Figure 6 illustrates a press **45** in which a quantity of thorium powder may be pressed into a pellet **46**, as by a plunger **47**, said powder resting on a plate **48** fitting the lower end of said

press 45. Pressures of about 20 tons per square inch are desirably applied.

Pressed pellets may be transferred to a crucible or cup 49 for the purpose of sintering or melting in vacuo. The only satisfactory refractory that we have found for melting is beryllia. In practice we have used crucibles 1½" at the top, 1" deep, with the bottom hemispherical. For protection in the event of its cracking, such a crucible is desirably set into an Alundum ignition capsule 51, 1¾" diameter by ¾" deep.

In order to obtain the necessary close coupling for heating by high-frequency induction, a 96% silica bottle 52 desirably 2½" outside diameter is used, with an appropriate high-frequency coil 53 which fits over the bottle with about ¼" clearance. During the melting operation, the capsule 51, supported crucible 49, and pressed pellet 46, preferably rest on an insulating refractory block 54 supported by a hollow refractory insulator 50 above a metal plate 12*a*, corresponding or identical with the plate 12 of Fig. 1, cooled and tubulated as in said first figure. The apparatus for melting may, therefore, be substantially identical with that used for reduction except that the argon line may be omitted.

With the oscillator available, we have been able to melt 300 gms. of thorium in one operation. This amount could be increased by insulation of the crucible containing the charge, or by increasing the size of the oscillator. During the melting operation, the pressed pellet 46 is placed in the crucible 49, as viewed in Fig. 7, and after the chamber 52 has been evacuated to 10 microns or less, the oscillator power is turned on through coil 53. If the powder is low in oxide content, the heating should take place instantaneously. Gas is evolved in the early stages of heating and this is pumped out continuously, shutting off the oscillator if the pressure exceeds approximately 50 microns.

When the metal becomes molten it is held in this condition until quiescent and completely liquid. The oscillator coil is then slowly raised with the current on, and the melt allowed to cool. The coil is raised slowly to reduce the tendency for blow holes to form in the melt during cooling. Some idea of the character of the metal may be obtained by observation of the condition of the melt. The molten metal should appear clear and relatively free from opaque particles. If the melt appears cloudy and viscous, probably due to oxide inclusions, the metal may not be satisfactory for cold working and will almost certainly show a tendency to edge crack. A convenient charge for the crucible and coil, as above described, is from 100 to 150 gms. Metal melted in a beryllia crucible contains traces of beryllia.

Fused buttons 60 of metal produced from pressed pellets 46 are partially spherical in shape because of the shape of the crucible. In order to convert these into a form suitable for rolling or swaging into wire, we have found that they can be reshaped under hydraulic pressure. To perform this operation, the buttons are placed in a steel die 55, with a recess somewhat larger than the original button, and of a shape desired. The associated plunger 56 is then operated to apply a pressure of between 30 and 60 tons per square inch to deform the button to the shape of the die. Buttons 1½" in diameter have been deformed in this manner into rods approximately ½" square. With good material, no edge cracks or other indication of severe working appears, and the metal could be extruded. Bars and discs

have been sintered using induction heating and similar vacuum techniques, as described under melting.

Thorium metal produced in accordance with our invention analyzes, as follows:

Thorium metal—about 99.5% to about 99.8%
Calcium <.005%
Molybdenum—about .005%
Iron—about .005%
Silica—about .01%

The remainder consists of thoria and spectroscopic traces of common metals including nickel, copper, and aluminum, and beryllia if melted in a crucible thereof.

Fig. 9 illustrates a pair of rolls 57 and 58 between which a plate 59 of thorium is being passed in order to reduce the thickness thereof, as in rolling plates of that metal.

Fig. 10 illustrates a die 61 through which a rod or wire of thorium is being drawn to the desired size.

From the foregoing it will be seen that we have devised an improved method of manufacturing thorium in which the reaction is carried out in a transparent bulb so that the progress thereof can be visually ascertained. By virtue of carrying out the reaction in a closed container and in an inert gas atmosphere, the product is protected from deterioration as the inert gas can neither escape during the reaction, nor air or other gas enter the container during cooling.

Although a preferred embodiment of our invention has been described, it will be understood that modifications may be made within the spirit and scope of the appended claims.

We claim:

1. The method of manufacturing thorium comprising mixing the oxide thereof with calcium, placing the mixture in a molybdenum cup, enclosing said cup in a high-silica glass bulb, evacuating said bulb, introducing inert gas thereinto, heating the cup and contents to between about 800° and 900° C. to melt the calcium and cause it to react with the oxide and liberate free thorium, cooling the mixture, leaching, and drying the powdered metal produced.

2. The method of manufacturing thorium comprising mixing the oxide thereof with calcium, placing the mixture in a molybdenum cup, enclosing said cup in a high-silica glass bulb, evacuating said bulb, introducing inert gas thereinto, heating the cup by high-frequency induction, first to about 700° C. and then to melt the calcium and cause it to react with the oxide and liberate free thorium, cooling the mixture, leaching, and drying the powdered metal produced.

3. The method of manufacturing thorium of an exceptionally high degree of purity, comprising mixing the oxide thereof with about 100% excess of granulated distilled calcium, placing the mixture in an open cup of high-melting point metal relatively inert to the charge and thorium at elevated temperatures, supporting said cup and surrounding it with a gas-tight enclosure to protect it and the thorium when produced from oxidation and make possible the employment of unusually high reacting temperatures, exhausting said enclosure to a high degree of vacuum, slowly heating said cup to about 700° C. by high-frequency induction to avoid substantially heating the enclosure, while pumping out the gas evolved, continuing the pumping operation to restore said high degree of vacuum, admitting to said enclosure, to a pressure slightly less than atmos-

pheric, a gas inert to the cup and its contents, then slowly again heating said cup by high-frequency induction to melt the calcium, starting a reaction, as noted by the appearance of a fine white mist, thus reducing the oxide to thorium powder, then by high-frequency induction increasing the temperature of said cup to about 1400° C. to increase the fluidity of the charge and quickly effect a reaction more complete than usual and holding it at said temperature for a moderate length of time, cooling and removing said cup from said enclosure, washing the admixed material from the thorium powder produced, and drying said powder.

4. The method of manufacturing thorium of an exceptionally high degree of purity, comprising mixing the oxide thereof with about 100% excess of granulated distilled calcium, placing the mixture in a cup of molybdenum, supporting said cup and placing it in a gas-tight enclosure to protect it and the thorium when produced from oxidation and make possible the employment of unusually high reacting temperatures, exhausting said enclosure to a high degree of vacuum, slowly heating said cup to about 700° C. by high-frequency induction to avoid substantially heating the enclosure, while pumping out the gas evolved, continuing the pumping operation to restore said high degree of vacuum, admitting to said enclosure, to a pressure slightly less than atmospheric, a gas inert to the cup and its contents, then slowly again heating said cup by high-frequency induction to melt the calcium and reduce the oxide to thorium powder, then by high-frequency induction increasing the temperature of said cup to about 1400° C. and holding it at said temperature to effect a reaction more complete than usual, cooling and removing said cup from said enclosure, washing the admixed material from the thorium powder produced, and drying said powder.

5. The method of manufacturing thorium comprising mixing the oxide thereof with calcium, placing the mixture in a cup of high-melting point material relatively inert to the charge and thorium at elevated temperatures, supporting said cup and placing it in a gas-tight enclosure to protect it and the thorium when produced from oxidation, exhausting said enclosure to a high degree of vacuum, slowly heating said cup to about 700° C., introducing inert gas into said enclosure, slowly again heating said cup to melt the calcium, starting a reaction and reducing the oxide to thorium powder, cooling and removing said cup from said enclosure, washing the admixed material from the thorium powder produced, and drying said powder.

6. The method of manufacturing thorium comprising mixing the oxide thereof with calcium, placing the mixture in a cup of high-melting point metal relatively inert to the chart and thorium at elevated temperatures, supporting said cup and placing it in a gas-tight enclosure to protect it and the thorium when produced from oxidation, exhausting said enclosure to a high degree of vacuum, slowly heating said cup to about 700° C. while pumping out the gas evolved, continuing the pumping operation to restore said high degree of vacuum, admitting inert gas to said enclosure to a pressure slightly less than atmospheric, heating the cup to above about 800° C. to melt the calcium and reduce the oxide to thorium powder, cooling and removing said cup from said enclosure, washing the admixed material from the thorium powder and drying said powder.

7. The method of manufacturing thorium comprising mixing the oxide thereof with calcium, placing the mixture in a cup of high melting point material relatively inert to the charge and thorium at elevated temperatures, supporting said cup and placing it in a gas-tight enclosure to protect it and the thorium when produced from oxidation, exhausting said enclosure to a high degree of vacuum, introducing inert gas to said enclosure, heating the cup and contents to melt the calcium, start a reaction, and reduce the oxide to thorium powder, increasing the temperature of said cup to about 1400° C. to increase the fluidity of the charge and quickly effect a reaction more complete than usual, cooling and removing said cup from said enclosure, washing the admixed material from the thorium powder produced, and drying said powder.

8. The method of manufacturing thorium comprising mixing the oxide thereof with calcium, placing the mixture in a cup of high-melting point metal relatively inert to the charge and thorium at elevated temperatures, supporting said cup and placing it in a gas-tight enclosure, exhausting said enclosure, introducing inert gas thereinto, heating the cup and contents to between about 800° and 900° C. to melt the calcium and cause it to react with the oxide and liberate free thorium, increasing the temperature of said cup to about 1400° C. to quickly effect a reaction more complete than usual and holding it at said temperature for a moderate length of time, cooling and removing said cup from said enclosure, washing the admixed material from the thorium powder produced, and drying said powder.

9. The method of manufacturing thorium comprising mixing the oxide thereof with calcium, placing the mixture in a cup of high melting point material relatively inert to the charge and thorium at elevated temperatures, supporting said cup within a gas-tight enclosure, evacuating said enclosure, introducing inert gas thereinto, heating said cup to melt the calcium, starting the reaction, and reducing the oxide to thorium powder, cooling the mixture, washing the admixed material from the thorium powder produced, and drying said powder.

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