

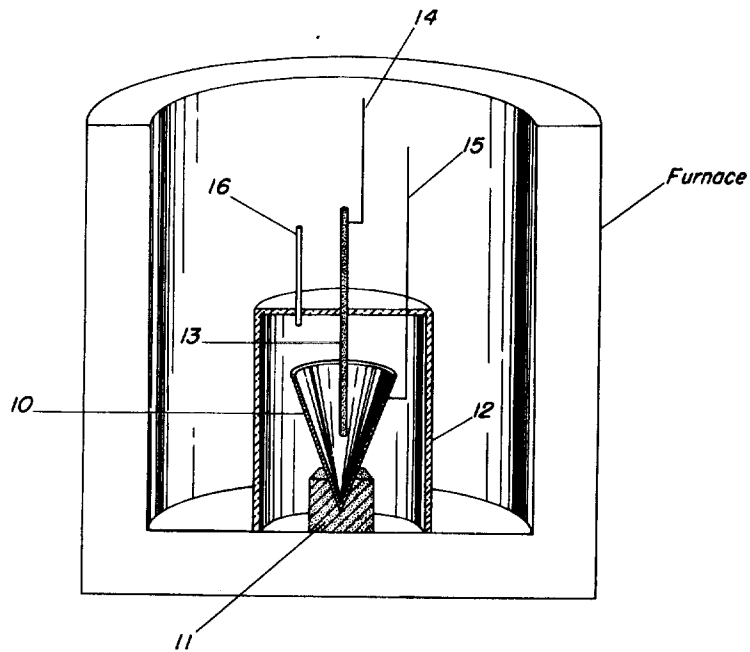
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PREPARATION OF PLUTONIUM

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WITNESSES:

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## PREPARATION OF PLUTONIUM

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This invention relates to methods for the electrodeposition of metals and more particularly to methods for the electrodeposition of plutonium.

It is desirable to prepare pure plutonium metal for many uses such as in neutron multiplying systems, neutronic reactors, experimental apparatus and the like. Pure plutonium may be produced by reducing plutonium compounds such as plutonium halides with an active metal. This, however, has the disadvantage that such reactions must be carried out at a temperature above the melting point of plutonium, thus increasing the danger of radioactive and toxic fumes resulting from the greater volatility of the plutonium at the advanced temperatures. This method has the further disadvantage that small amounts of impurities are easily introduced.

The primary object of this invention is, therefore, to provide a method for preparing pure plutonium.

Another object of this invention is to provide a method for efficiently preparing pure plutonium at a relatively low temperature.

Still further objects and advantages of this invention will appear in the following description including the drawing hereby made a part of the specification wherein the figure is a cross-sectional schematic of the apparatus of Example II.

The objects of this invention are achieved by the electrolysis of a fused bath containing a plutonium halide. A number of different plutonium halides may be used in the fused bath as the source of the plutonium but the chlorides are more desirable than the other halides because they are relatively non-hygroscopic and have relatively low melting points. Of the plutonium chlorides, the trichloride is the preferred because it is readily made, it is less hygroscopic than the plutonium tetrachloride, and the yield obtained when it is used for electrolysis is less affected if some moisture is present.

An alkali metal halide or an alkaline earth metal halide or mixtures of such halides are advantageously used in the fused bath as an auxiliary metal or metals because these alkali metals and alkaline earth metals are more electropositive than plutonium. It is preferable that the auxiliary metal halide or halides used in the bath have the same negative ion as the plutonium halide, and that the bath have a low melting point. As an example of such a bath, a mixture of plutonium, barium, potassium, and sodium chlorides is very satisfactory because it has a rather low melting point. It is possible to prepare other baths with lower melting points, such as a mixture of plutonium, lithium, potassium, and sodium chlorides. A low melting point bath permits operation at a lower temperature with non-porous containers, vitreous or metallic, in place of the graphite containers needed at the higher temperature ranges. This prevents losses due to the relatively greater porosity of the graphite. It is, of course, necessary that the containers do not soften at the temperature used and do not alloy with plutonium. As an example of containers which have the desired prop-

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erties, containers of tantalum, molybdenum, tungsten, chrome-nickel alloys or silver may be used.

It is desirable that the bath not be operated at too low a temperature because this may permit some of the other metals to deposit with the plutonium and thus contaminate it.

The method of the invention can best be illustrated by the following examples which are given for this purpose only and not for the purpose of limiting the spirit or scope of the invention.

*Example I*

Approximately ten grams each of reagent grade barium chloride, potassium chloride, and sodium chloride are thoroughly dried until all the moisture, including the water of crystallization, if any, is removed. Each salt is then individually fused in platinum and cast in an inert metal vessel such as a platinum vessel. The salts are ground in a porcelain mortar. 2.4 grams of barium chloride, 1.55 grams of potassium chloride and 1.05 grams of sodium chloride, are thoroughly mixed, fused together, and reground. The mixture is kept in a desiccator and heated to 150° C. before use. Two tungsten rods 0.040 inch in diameter are connected to the anode and cathode leads which are 0.38 inch apart and which extend through the top of a Pyrex container. The Pyrex cell is evacuated and flushed with argon which has been dried and purified. The rate of flow of the argon is adjusted to a constant value to prevent the oxidation of the plutonium, which occurs rapidly, especially at higher temperatures. 300 milligrams of the mixed salt and 59.4 milligrams of dry oxychloride-free plutonium trichloride are then introduced into the cell in a drybox and the mixture is heated to 600° C. by means of the furnace which surrounds the container. When the bath is molten the anode and cathode are lowered into the bath and a current of 0.20 ampere is maintained for 25 minutes at a potential of about 5 volts while the temperature is maintained at about 600° C. The current and the furnace are turned off, and the cell is cooled in the presence of argon. The argon is then turned off.

Upon opening the cell, the plutonium is found to be in the form of a powder with some particles weighing from 3 to 4 milligrams. The recovery exceeds 50 percent and the plutonium assays 100 percent plutonium.

The temperature of 600° C. used in this example, is considerably less than that used in chemical conversion of plutonium above its melting point, and the dangers of toxic and radioactive fumes is therefore much less.

When it is desired not only to purify the plutonium, but also to obtain it in the form of a single massive piece of metal instead of in the form of individual particles, it is desirable to use a higher temperature than the 600° C. used in Example I. The reduction at higher temperatures is not performed in Pyrex. Instead, a metal cell, such as one of those mentioned hereinbefore, is satisfactory for such a use. The operation at a higher temperature is illustrated in Example II, which presents the presently preferred embodiment of the method of the invention using one such metal container.

*Example II*

About 5 grams each of reagent grade barium chloride, potassium chloride, and sodium chloride are thoroughly dried, fused, cast and ground. 1295 milligrams of barium chloride, 838 milligrams of potassium chloride and 567 milligrams of sodium chloride are thoroughly mixed, fused together, and reground to give a mixture of 48 percent barium chloride, 31 percent potassium chloride and 21 percent sodium chloride. The mixed salt and 1432 milligrams of dry plutonium trichloride, free of oxychlorides, are placed in a conical molybdenum cell 10,

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see the figure, in the form of an inverted cone having an open top which rests on a graphite platform 11 and which is entirely enclosed in a Vycor jacket 12. (The composition of Vycor is disclosed in Journal of Research of the National Bureau of Standards, vol. 26, 538 (1941)). A graphite rod 13, 0.25 inch in diameter extends into the top of the cell and is connected to an anode lead 14. The molybdenum cell is connected to a cathode lead 15. The system is evacuated and flushed with hydrogen through inlet 16, such hydrogen having been previously purified by passing over uranium chips at 500° C. and been dried by passing through a train consisting of a cold trap and a soda-lime and silica gel drying tower. The flow of hydrogen is continued during the processing, i.e., the hydrogen flows into the jacket through inlet 16 and out of the jacket between the bottom surface of jacket 12 and the furnace. The furnace may be of any type well known in the art. The hydrogen, like the argon used in Example I, prevents the oxidation of the plutonium. The bath is raised to a temperature of about 600° C. The temperature is maintained by means of the furnace; the graphite rod is lowered into the bath and the temperature of the bath is raised to 800° C. while a current of 2.0 amperes is applied with a potential of about 5 volts. Complete electrolysis usually takes about 20 minutes. The current and the furnace are turned off. The cell is cooled in the presence of hydrogen and the hydrogen is turned off. The salt is cleanly dislodged from the cell wall and is yellow-white in color. The product is in the form of a well-collected single button of pure plutonium which has the melting point of pure plutonium, the density of pure plutonium, and assays 100.0 percent pure plutonium. Microscopic study indicates that there is no evidence of alloying at the interface of the plutonium and the molybdenum cell. The recovery of plutonium is usually greater than 75 percent.

For maximum efficiency, all materials entering the cell, particularly the plutonium halide, should be thoroughly dry and the plutonium halide should be free of oxyhalides. When one of the plutonium chlorides is used, this may be accomplished by placing the plutonium compound in a stream of dry hydrogen chloride at a temperature below 80° C. until all moisture disappears, increasing the temperature of the bath to about 280° C., and maintaining it at this value for several hours.

Many embodiments of the method of this invention are possible. For example, helium gas or the like may be used as the non-oxidizing atmosphere during and after the electrolysis in place of or along with the argon used in Example I or the hydrogen used in Example II. The hydrogen has the feature of combining with the halogen released at the anode, thereby reducing its corrosiveness.

As pointed out hereinbefore, it is possible to use other trihalides or tetrahalides of plutonium in place of the plutonium trichloride. For example, plutonium tetrachloride or plutonium tetrafluoride may be used. It is also possible to use as auxiliary metals in the bath other halides of the alkali or alkaline earth metals. For example, a bath consisting of the fluorides or mixtures of chlorides and fluorides of barium, potassium, and sodium may be used.

It may be noted that in the examples the initial concentration of the plutonium trichloride was 16.6 percent in Example I and 34.7 percent in Example II. This concentration may, of course, be varied through a rather wide range. When working on a small scale a high initial concentration of plutonium causes an excessive reduction in the volume of the salt bath during electrolysis. Spray and evaporation losses are also increased with increase in concentration of the plutonium. On the other hand, a very low initial concentration does not yield as satisfactory deposits of plutonium. Efficient results may be obtained from a bath containing from 5 to 75 percent by weight plutonium, but the preferred initial concentration

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is from 30 to 40 percent by weight. It has been found possible to continue electrolysis to the point where virtually no plutonium salt remains in the electrolyte.

In like manner, although the graphite used as anode in Example II is not appreciably affected by the bath, the tungsten anode used in Example I may be used if all possibilities of carbon contamination are to be removed. The cathode may be of tungsten as in Example I, molybdenum as in Example II or other metals which are not appreciably soluble in the electrolyte, e.g., tantalum.

The temperature of the bath may also be varied within rather wide limits. It may be as low as 600° C., the temperature of the bath in Example I, or as high as 850° C. However, the range 750° C. to 850° C., is preferable, and a temperature of about 800° C. has been found to give the best results.

The current may also be varied considerably. At a given current density, the recovery is reduced by an increase in temperature. This is to be expected because the cathode efficiency is reduced almost to zero by reaction of anode products with the metal. However, the recovery may be increased at constant temperature by increasing the current density. Current densities as high as 100 amperes per square inch have been satisfactorily used.

The process can of course be carried out on a larger scale. The cell construction can be readily changed by methods well known to those skilled in the art to provide for continuous production. This process has high current efficiency and low operating costs.

Because there are so many embodiments of the method of this invention, it is to be understood that this invention is not to be limited except as indicated in the appended claims.

What is claimed is:

1. The process which comprises electrodepositing plutonium under non-oxidizing conditions from a fused bath consisting essentially of from 5 to 75 percent plutonium halide, said plutonium halide being thoroughly dry and free from oxyhalides, and at least one halide of a metal of the class consisting of alkali metals and alkaline earth metals, said fused bath being at a temperature between 600° C. and 850° C.

2. The process which comprises electrodepositing plutonium under non-oxidizing conditions from a fused bath consisting essentially of from 5 to 75 percent plutonium halide, said plutonium halide being thoroughly dry and free from oxyhalides, and at least one alkali metal halide, said bath being at a temperature between 600° C. and 850° C.

3. The process which comprises electrodepositing plutonium under non-oxidizing conditions from a fused bath consisting essentially of from 5 to 75 percent plutonium halide, said plutonium halide being thoroughly dry and free from oxyhalides, and at least one alkaline earth metal halide, said bath being at a temperature between 600° C. and 850° C.

4. The process which comprises electrodepositing plutonium under non-oxidizing conditions from a fused bath consisting essentially of from 5 to 75 percent plutonium trichloride, said plutonium trichloride being thoroughly dry and free from oxychlorides, and at least one alkali metal chloride and at least one alkaline earth metal chloride, said bath being at a temperature between 600° C. and 850° C.

5. The process which comprises electrodepositing plutonium under non-oxidizing conditions from a fused bath consisting essentially of from 30 to 40 percent plutonium trichloride, said plutonium trichloride being thoroughly dry and free from oxychlorides, and at least one chloride of a metal of the class consisting of alkali metals and alkaline earth metals, said bath being at a temperature between 750° C. and 850° C.

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6. The process which comprises electrodepositing plutonium under non-oxidizing conditions from a fused bath containing from 5 to 75 percent plutonium trichloride, said plutonium trichloride being thoroughly dry and free from oxychlorides, and the balance of barium chloride, potassium chloride and sodium chloride, said bath being at a temperature between 600° C. and 850° C.

7. The process which comprises electrodepositing plutonium under non-oxidizing conditions from a fused bath containing from 30 to 40 percent plutonium trichloride, said plutonium trichloride being thoroughly dry and free from oxychlorides, and the balance of a mixture of 48 percent barium chloride, 31 percent potassium chloride and 21 percent sodium chloride, said bath being at a temperature of about 800° C.

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