United States Patent [19]

Mosley, Jr. et al.

[11] **3,873,651**

[45] **Mar. 25, 1975**

[56] **References Cited**

UNITED STATES PATENTS

3,281,371	10/1966	Nerge et al.	252/301.1 R
3,422,167	1/1969	Bowman	264/0.5
3,488,502	1/1970	Dukes	250/106 S
3,516,935	6/1970	Monforte et al.	34/5 X
3,567,943	3/1971	Wallhansen	250/106 S
3,627,691	12/1971	Boulogne et al.	252/301.1 R
3,640,888	2/1972	Baybarz et al.	252/301.1 R
3,697,329	10/1972	Bunker et al.	250/106 S X

OTHER PUBLICATIONS

McDonnell et al., "Preparation of Industrial ^{252}CF Neutron Sources . . .," Nuc. Sci. Abst., Vol. 25, No. 21, Nov. 1971, No. 50600.

[57] **ABSTRACT**

A solution containing radioisotope and palladium values is atomized into an air flow entering a cryogenically cooled chamber where the solution is deposited on the chamber walls as a thin layer of frozen material. The solvent portion of the frozen material is sublimated into a cold trap by elevating the temperature within the chamber while withdrawing solvent vapors. The residual crystals are heated to provide a uniformly mixed powder of palladium metal and a refractory radioisotope compound. The powder is thereafter consolidated into a pellet and further shaped into rod, wire or sheet form for easy apportionment into individual radiation sources.

4 Claims, 2 Drawing Figures

ᖷᎮᏩ - 1
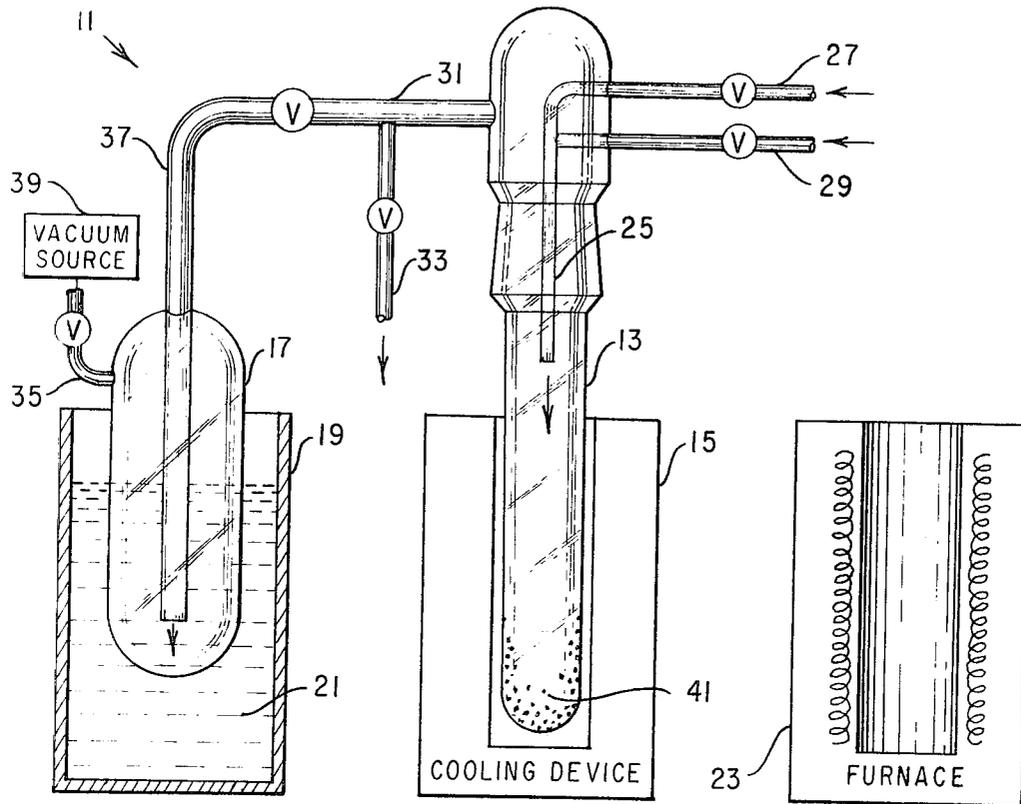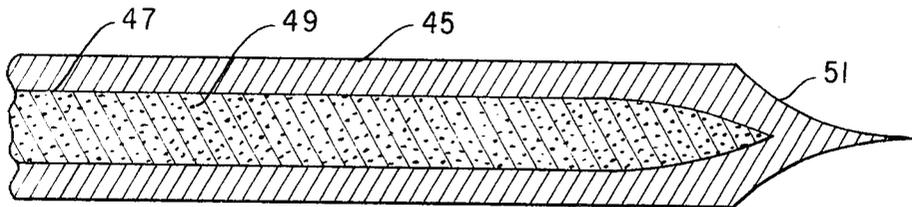
ᖷᎮᏩ - 2

FREEZE DRYING METHOD FOR PREPARING RADIATION SOURCE MATERIAL

BACKGROUND OF THE INVENTION

The present invention was made in the course of, or under, a contract with the United States Atomic Energy Commission.

Field of the Invention

The present invention relates to radiation source materials, particularly those including rare and expensive radioisotopes. For example, the spontaneous fission of californium-252 provides a substantial neutron flux but this element is extremely difficult and expensive to produce and fabricate. This element is produced by the long and costly procedure of successive neutron capture in nuclear reactors, beginning with, for instance, uranium-238. Handling this radioisotope is both difficult and hazardous due to neutron fission fragments and alpha emissions. Consequently, californium-252 must be provided in a material form that can be conveniently and safely allotted into precise microgram and milligram quantities for encapsulation as a neutron source with a minimum of process loss. In respect to safety, this isotope must be contained in a refractory and stable form to prevent its escape should the encapsulation fail during use or storage.

Similar problems arise in the production and containment of radiation sources from other radioisotopes. Actinides such as actinium-227, plutonium-238, curium-242 or 244, americium-241 or 243 as well as other transplutonium isotopes have potential as heat, gamma, beta and alpha sources. Like californium-252 these isotopes are produced by the costly process of neutron capture in a nuclear reactor. Other useful radiation source isotopes such as polonium-210 and cobalt-60 are similarly produced. Fission and decay products including cesium-137, strontium-90, thulium-170 or 171 and promethium-147 also have use as radiation sources and like the above-mentioned isotopes, are difficult to separate, handle and contain safely.

Description of Prior Art

Prior radiation source materials have included salts of radioisotopes in solution, in precipitate or oxide form. Californium-252, for instance, can be transferred or stored in an acidic aqueous solution of californium nitrate, as a californium oxalate precipitate, perhaps including a carrier metal oxalate, or as californium oxide or oxysulfate obtained by incinerating an ion exchange resin containing californium ions. The allocation of a californium material in any of these forms into precise quantities followed by encapuslation to a form usable as neutron sources can be a difficult process if losses are held to an extremely small level as required. Moreover, inconvenient wet chemistry procedures may be required in the purification and encapuslation of each californium neutron source from these prior art material forms. For example see SRO—153 "Guide for Fabricating and Handling [252]Cf Sources" pp. 43–59, 1971, available from National Technical Information Service, U.S. Department of Commerce; and U.S. Pat. No. 3,627,691 to Boulogne et al.

One method of preparing a californium-252 neutron source or other radiation source material is described in the assignee's copending application Ser. No. 158,999(70) filed July 1, 1971. This earlier method in-

cludes blending a solution containing californium values with noble metal powder followed by drying and forming the powder into the desired integral shape. Unfortunately yields, that is californium in the final product as a percentage of californium in the feed solution, have exceeded 90 percent only in isolated cases. Generally yields of only about 60–75 percent have been obtained although substantially all of the californium has been recovered and recycled by leaching the process vessels and tools with dilute nitric acid solution. One of the reasons for these relatively low yields is that liquid splattering results from boiling and radiolytic gasing as the liquid becomes concentrated during evaporation.

SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to provide an improved method of preparing a quantity of radiation source material having a uniform distribution of a radioisotope within a matrix material for convenient apportionment into individual radiation sources.

It is also an object to provide a method of preparing radiation source material which minimizes loss of ratioisotope arising from mechanical mixing of powder, liquid boiling and radiolytic gasing.

It is a further object to provide a method of preparing neutron source material in which a high percentage yield of californium will be obtained in the product in respect to the californium present in the feed material.

In accordance with the present invention a liquid solution containing a uniform mixture of pallidium and californium isotope values is atomized into a liquid mist entrained within an air flow. The mist is sprayed into a vessel cooled to a sufficiently low temperature to freeze a thin layer of solid crystals onto the inside vessel walls. A substantial portion of the solvent is sublimated from the crystals by withdrawing solvent vapors from the vessel while maintaining the crystals at a temperature below their melting point. The residual crystals are then heated to remove the solvent associated with crystalization and to dissociate the califorium isotope and palladium values to refractory and elemental forms. The resulting powder, comprising a uniform dispersion of the refractory californium isotope throughout the palladium metal, can be consolidated into an integral form and further shaped into a rod, wire or sheet for convenient apportionment into individual radiation sources.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic showing of one apparatus that can be employed in practicing the present invention.

FIG. 2 is an illustration of one form of radiation source material that can be produced by the method of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to FIG. 1, the apparatus is shown with an assembly 11, including a first vessel 13 removably disposed within a cooling device 15 and a second vessel 17 partially submerged in a container 19 of refrigerant 21. This particular arrangement of the apparatus is employed in performing one of the several steps of the present method which will be described hereinafter. In this regard a furnace 23, adapted to receive and heat vessel 13 is shown for use in a subsequent step.

Assembly 11 includes an injection tube 25 having manifold inlets 27 and 29 for gas and liquid feed solutions. Tube 25 is directed to discharge towards the lower wall surfaces of vessel 13, but extends only part way down the vessel to a point sufficiently spaced from the bottom to avoid splattering. An outlet tube 31 communicates with the top portion of vessel 13 and branches into a valved vent outlet 33 and a valved inlet tube 37 extending into second vessel 17. Inlet tube 37 is directed to discharge towards and near the lower, cold surfaces of vessel 17 to freeze and trap condensible material as a deposit of ice. A vacuum source 39 is connected through a valved conduit 35 to the inner volume of vessel 17 to evacuate noncondensible gases from within the assembly during sublimation.

Where only milligram and gram quantities of material are to be processed, assembly 11 can be laboratory type implements as illustrated. Vessel 13 can be adapted for positioning within cooling device 15 as shown, within furnace 23 or refrigerant container 19 for performing the several process steps.

Various types of heating and cooling means illustrated at 15, 21, and 23 can be selected. Refrigerant 21 within container 19 is one that is capable of maintaining a very low cryogenic temperature such as liquid nitrogen or dry ice and acetone. Cooling device 15 can be a more moderate source of refrigeration such as a thermoelectric cooler or a liquid ammonia or freon cooled device. It is sufficient for device 15 to maintain a cold temperature that is several degrees centigrade below the melting point of the material to be freeze dried. Furnace 23 can be a conventional electric or other type furnace that can produce temperatures of several hundred degrees centigrade.

In one manner of performing the method of the present invention, vessel 13 is placed within container 19 in contact with refrigerant 21 maintained at a cryogenic temperature. A solution or slurry containing palladium valves, and a dissolved or colloidally dispersed californium isotope salt, such as californium nitrate or oxalate, is introduced into inlet 29 of injection tube 25. The solution can include water, an alcohol or some other suitable liquid substance as a solvent. An inert gas or air is simultaneously introduced into inlet 27 to atomize the solution into a mist as it is sprayed from tube 25 towards the lower walls of vessel 13. The walls of vessel 13 are maintained at a temperature substantially below the freezing point of the solution to effect rapid and complete freezing of the solution as a thin layer of frozen crystals on the vessel walls. The frozen crystals include dissociable salts of the californium isotope and palladium, as well as the solvent from the original solution. The dry inert gas flow is continuously withdrawn through vent outlet 33 with valved inlet tube 37 closed while the freezing operation is being performed.

After the solution is frozen onto the vessel walls, remelting must be prevented to avoid nonuniformity in the product. For this reason, thin frozen layers, e.g., about 0.1 to 0.5 millimeters, are preferred to allow removal of the heat generated in radioisotope disintegration before the central portion of the layer remelts. In addition, the relatively large exposed surface of the thin layer of frozen solution is beneficial in performing the following vacuum drying step.

During vacuum drying, vessel 13 is disposed in cooling device 15 and the second or trap vessel 17 is partially submerged in refrigerant 21 as is shown in FIG. 1. The temperature of vessel 13 is elevated to a level just several degrees centigrade below the melting point of the solution. Valved inlet tube 37 is opened with vent outlet 33 closed to draw solvent vapors from vessel 13 into trap vessel 17. Vacuum source 39 is engaged to evacuate the assembly to a few millimeters of mercury absolute pressure. Solvent vapors discharged from inlet 37 will contact the cold lower surfaces of trap vessel 17 and freeze, thus capturing any of the radioisotope that may be entrained with the vapors. As a result of this operation, the solvent within the frozen solution is sublimated into trap vessel 17 leaving crystals of hydrated salts 41 having a uniform distribution of dissociable californium isotope salt and palladium salt within vessel 13.

Drying of crystals 41 is completed by transferring vessel 13 to furnace 23 and slowly warming to a temperature of between about 100° to 300°C. A flowing inert gas is introduced into inlet 27 and discharged through vent outlet 33 to remove solvent vapors from the assembly. During this drying step at elevated temperature, the water or solvent bound within the hydrated salt crystals is removed to leave a dry salt residue of powder consistency.

After the salt is dehydrated, the gas flow is changed to a slightly reducing composition, for instance 4% H_2—96% He gas, and the temperature elevated to a sufficient level to dissociate the palladium salt to the elemental state and the californium isotope salt to a refractory form such as an oxide. The volatile portions of the salt or salts are discharged with the gas flow through outlet 33 as this step is performed.

The powder from the above dissociation step is shaped by metallurgical processes to form a pellet, rod, wire or sheet. The powder is compacted into a pellet and heated to a temperature just below where significant sintering begins in a slightly reducing atmosphere. This heating step ensures that all of the salt has dissociated to refractory and elemental form before the palladium metal matrix is closed by sintering. The pellet is then heated to a sufficient sintering temperature in an inert gas atmosphere to fuse the palladium metal particles together in an integral matrix. The completed pellet will contain a uniform dispersion of the californium isotope sealed within the palladium metal matrix and can be encapsulated either along or with other pellets for use as a radiation source. If desired, the pellet or pellets can be enclosed within a tubular sheath of noble metal and elongated by rolling, swaging, drawing or other shaping processes into a rod or wire form with a noble metal cladding. Various cross sectional configurations such as circular, square, rectangular, etc., can be adopted for the pellet, rod or wire members. Sheets of radiation source material can be provided by suitable rolling or pressing processes.

FIG. 2 illustrates a rod or wire form of the radiation source material. An outer cladding 45 of noble metal protects and contains an inner core 47 of palladium metal matrix and refractory californium isotope material. Small particles 49 of the californium isotope in refractory form are shown uniformly dispersed throughout the palladium metal matrix. A measured length of this wire can be removed with a conventional pinch cutting tool having rounded edges such as one used in pinch welding. A sealed end portion as shown at 51 can thereby be provided both on the severed length and the

5

remainder of the wire. The severed length of wire can be encapsulated to provide a radiation source of predictable strength.

The following examples are presented to illustrate specific procedures and materials for preparing radiation sources in accordance with the present invention. It will be clear, however, that variations in materials, quantities and procedures can be employed within the scope of the invention.

EXAMPLE I

A solution containing 10 grams of palladium tetramine dinitrate, 10 milligrams of samarium nitrate and 5 nanograms of californium-252 in about 50 cc water was prepared and atomized into a mist within a flowing air stream. The mist was rapidly frozen into a thin solid layer on the lower portion of a vessel cooled by liquid nitrogen at about $-196°C$. The resulting frozen crystals were allowed to warm to $-10°C$ and maintained at this temperature for about 10 hours while withdrawing solvent vapors from the vessel at an absolute pressure of less than 2 mm. mercury. The solvent vapors were passed into contact with cold surfaces of a water trap vessel submerged in liquid nitrogen at about $-196°C$. As a result of this treatment most of the water was sublimated from the crystals into the cold trap. However, none of the californium or samarium was discovered in the cold trap. The residual hydrated crystals were heated to $200°C$ in flowing argon for 30 minutes to complete the drying operation. Then the atmosphere was changed to 4% H_2—He and the temperature raised to $450°C$ for 1 hour to dissociate the samarium and californium nitrates to oxides and the palladium tetrammine dinitrate to palladium metal. The resulting powder was pressed at 15,000 psi to form a cylindrical pellet, heated to $1000°C$ in 4% H_2—He gas and sintered on an alumina setter at $1300°C$ in argon for 30 minutes. The sintered pellet was enclosed in a palladium metal sheath and swaged into a 25 cm. long wire of about 1 millimeter square cross section in several reduction steps interspersed with annealing at $800°C$ in argon. The wire was found to have both samarium and californium distributed along its length to within less than 5 percent deviation from uniformity. Moreover, substantially 100 percent of the californium and samarium within the feed solution was detected within the final wire product.

EXAMPLE II

A similar procedure to that of Example I is performed with about 1 gram of palladium as nitrate, 5 milligrams of californium-252 in nitrate solution and no samarium in the feed solution. An approximately 10 centimeter long palladium clad wire is produced having a substantially uniform distribution of californium along its length.

EXAMPLE III

A low intensity neutron source material is provided without introducing a carrier element in addition to the californium and palladium. A slurry containing about 5 grams of palladium nitrate and less than 10 nanograms of californium nitrate is prepared and processed as in Example I. A palladium clad wire having a uniform neutron emission of about 10^3 neutrons/cm-sec throughout its length is produced.

6

Although isotopes of elements other than californium and samarium have not been tried in this process, it is reasonable to assume that a large number of other radioisotopes could be processed by the present method. Any radioisotope which forms a refractory compound on the decomposition of a dissociable salt could most probably be employed. Most lanthanides and actinides, as well as other metallic cations, form soluble nitrate solutions and nitrate salts crystalized from these solutions can be dissociated to refractory oxides. Salts other than nitrates such as carbonates, and phosphates might also be used in some instances. For example a colloidal dispersion in solution of cesium, noble metal and uranyl carbonates could be frozen to form crystals which could then be thermally dissociated into water, carbon dioxide gas and powder particles having a uniform distribution of $Cs_6U_2O_7$ within palladium metal.

Noble metal cations other than palladium, for instance platinum, ruthenium, rhodium, silver, osmium, iridium, and gold can be crystallized from solution along with the radioisotope salt in practicing the present invention. However, palladium has been found to be a preferred matrix material for use in a radiation source after consideration of numerous properties of this noble metal. For instance, palladium resists oxidation, has a high melting point ($1552°C$), alloys readily with californium and other elements, is ductile, dissolves in concentrated nitric acid for recovery of the radioisotope, gives little gamma interference on neutron activation, and is less expensive than many other noble metals.

It will be seen that the method of the present invention can be used to prepare radiation source materials of uniform intensity including neutron, gamma, beta, alpha, heat or a combination of various type sources. The method reduces the risk of contamination associated with other methods employing the blending of dry powders or of blending powders with solutions. A high yield of the radioisotope from feed to product is obtained even in the preparation of low intensity sources due to the complete freezing of substantially all of the feed solution and the gentle process of removing the solvent therefrom by sublimation. The radiation source material produced by the present method will include a radioisotope in refractory form uniformly dispersed and sealed within a stable noble metal matrix material. A measured portion of the material can be subdivided and encapuslated for use in an individual radiation source of predictable strength. The source will in most instances safely contain the radioisotope even if the encapsulation should fail since the radioisotope is in the form of a refractory compound trapped within an inert noble metal matrix.

What is claimed is:

1. A method of preparing radioisotopic source material comprising:

    a. atomizing a liquid solution of palladium and californium isotope values into an air flow to form a liquid mist;

    b. freezing said mist to form a layer of solid crystals including, within a solid solvent, a uniform mixture of said californium isotope and said palladium as dissociable salts;

    c. withdrawing solvent vapors from above said crystals to sublimate said solvent from said mixture of salts;

d. heating said crystals to a sufficient temperature to decompose said mixture of dissociable salts to a uniform mixture of palladium metal and refractory californium isotope compound;

e. consolidating said uniform mixture into a pellet;

f. sintering said pellet to close said palladium metal into a matrix containing said refractory californium isotope compound; and

g. shaping said sintered matrix into an elongated member that includes a uniform dispersion of said refractory californium isotope compound throughout the length of said palladium metal matrix.

2. The method of claim 1 wherein the step of freezing said mist is performed at a first temperature substantially below the melting point of said crystals and the step of withdrawing solvent vapors is performed while maintaining said crystals at a second temperature between said first temperature and the melting point of said crystals.

3. The method of claim 1 wherein said dissociable salts are nitrates and said refractory californium isotope compound is an oxide.

4. The method of claim 1 wherein said californium isotope is californium-252.

* * * * *