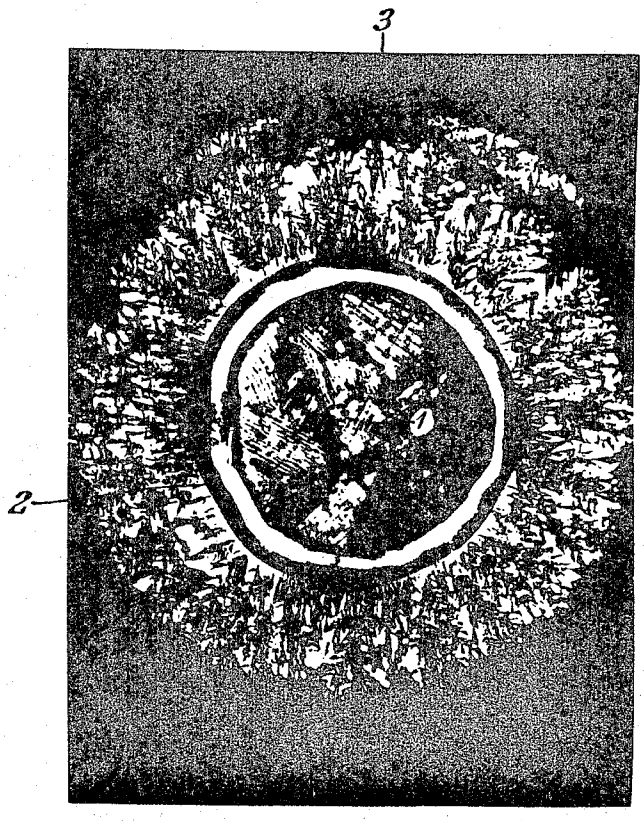
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RADIOACTIVE SPHEROIDS COATED WITH PYROLYTIC GRAPHITE

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RADIOACTIVE SPHEROIDS COATED WITH PYROLYTIC GRAPHITE

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Original application Dec. 18, 1962, Ser. No. 245,512, now Patent No. 3,247,008, dated Apr. 19, 1966. Divided and this application Dec. 28, 1965, Ser. No. 516,862

3 Claims. (Cl. 176—67)

This application is a division of application Serial No. 245,512, entitled, "Process for Coating Radioactice Spheroids With Pyrolytic Graphite," filed December 18, 1962, now U.S. Patent No. 3,247,008.

This invention relates to a process for coating radioactive particles with pyrolytic graphite by pyrolysis of hydrocarbons at temperatures in excess of 1800° C., and to nuclear fuel particles having a coating of pyrolytic graphite.

Radioactive materials, particularly uranium and uranium compounds, are subject to certain disadvantages which must be overcome when these materials are used in the form of small spheroids embedded in a graphite body, thereby constituting a nuclear fuel element. For example, nuclear fuel particles, particularly small particles, are subject to severe oxidation due to the environment in which they are used. Another disadvantage is that uranium has a tendency to migrate through a conventional graphite matrix at elevated temperatures. These disadvantages can be conveniently overcome by coating the particles with some suitable substance which is relatively impermeable and resistant to high temperatures.

Because of its low thermal neutron cross section, relative inertness, low permeability, high sublimation point and low susceptibility to radiation damage, pyrolytic graphite is eminently suited as a coating material for nuclear fuel particles. It has been found that pyrolytic graphite coatings deposited at relatively high temperatures are particularly effective in minimizing the aforementioned disadvantages. However, nuclear fuel particles cannot be heated directly to temperatures which are high enough to provide optimum coating characteristics due to the tendency of the particles to fuse to themselves and to the container walls at such temperatures.

Therefore, it is an object of this invention to provide a process for coating nuclear fuel particles with pyrolytic graphite at temperatures above the surface sintering of the radioactive particles wherein adhesion of the particles to themselves and to the coating chamber wall is avoided. It is another object to provide the particles with a high density, high strength barrier with which to retain the gaseous fission products of these radioactive materials. It is a further object to minimize undesirable oxidation of the fuel particles. A still further object is to substantially reduce migration of uranium through the graphite matrix of the fuel element at elevated temperatures.

These and other related objects are achieved by depositing on the radioactive particles a thin layer of laminar pyrolytic graphite at a temperature slightly below the surface sintering temperature of the radioactive material and then raising the temperature substantially above the surface sintering temperature thereby commencing the deposition of a final relatively thick layer of columnar pyrolytic graphite.

This process which results in a dual layered coating of pyrolytic graphite is applicable to particles of uranium carbide which have a surface sintering temperature below 1800° C. as well as to materials having a surface sintering temperature above 1800° C., e.g., thorium carbide.

The term surface sintering as used herein, including the appended claims, represents the temperature at which the surface of the particles coalesce, fuse or otherwise bond together or to the coating chamber walls. The surface sintering temperature is dependent, at least in part, on the nature of the particulate radioactive material and on the size of the particles.

The laminar layer of pyrolytic graphite is characterized as not having a crystalline structure while the columnar pyrolytic graphite has a distinct crystalline structure visible through the use of polarized light.

This process is intended to provide a thick outer coating of columnar pyrolytic graphite having a density of at least 1.8 grams per cubic centimeter.

In the practice of the instant invention pyrolytic graphite is deposited on radioactive particles by placing the particles in a suitable container and heating them to a temperature slightly below the surface sintering point of the radioactive particles while surrounding the particles with an atmosphere composed of an inert gas and a gaseous hydrocarbon. The elevated temperature causes the hydrocarbon gas to crack or pyrolyze thus depositing free carbon atoms on the surface of the radioactive particles.

The particulate radioactive material is preferably kept in motion while the pyrolytic graphite is being deposited by some suitable means such as a rotating capsule, a fluidized bed or a vibrating surface. This insures that the entire surface of each particle is exposed to the hydrocarbon gas and thus provides for a uniform coating of pyrolytic graphite. Once the initial thin layer of pyrolytic graphite has been deposited the temperature is raised above the surface sintering temperature of the radioactive particles and the deposition continued until a coating of the desired thickness is built up. The final coating can be applied at temperatures ranging from about 1800° C. to about 2200° C.

The coating process is preferably interrupted after the deposition of the initial thin layer of graphite, and the particles are then removed from the coating chamber and washed with an aqueous solution of a strong acid such as nitric acid, hydrochloric acid, sulfuric acid, and the like, at an elevated temperature, preferably from 90° C. to about 98° C. This serves to eliminate any surface contamination and also to dissolve any particles which may be uncoated and therefore would tend to sinter at high temperatures. The cleaned particles are then replaced in the coating chamber and heated to the desired temperature and the final outer coat of pyrolytic graphite deposited.

The rate of deposition of both the inner and outer layer can be conveniently regulated by adjusting the concentration of the hydrocarbon gas in the container and the rate at which the gases, i.e., the hydrocarbon gas and the inert gas, flow through the air tight container. Preferably the gas mixture is composed predominantly of an inert gaseous diluent such as argon, helium or hydrogen. The temperature at which the deposition is carried out is also a factor which influences the rate of deposition. Finally the period of time for which the low temperature

deposition is maintained may be varied in order to control the thickness of the several layers of pyrolytic graphite.

Any hydrocarbon which will pyrolyze to provide free carbon atoms at a temperature below the surface sintering point of the radioactive particles can be employed for the deposition of the initial layer of pyrolytic graphite. The same or a different hydrocarbon may be used for the high temperature deposition of the outer coating. Suitable hydrocarbons include aromatic hydrocarbons such as benzene; aliphatic hydrocarbons such as the alkanes, e.g., methane, ethane, propane, butane, and the like; the alkenes, e.g., ethylene, propene, butene, pentene and the like, alkylenes, e.g., acetylene; cycloaliphatic hydrocarbons such as cyclobutane, cyclopentane, cyclohexane, cyclobutene, cyclopentene can also be used. Preferred hydrocarbons are the low alkanes having up to 10 carbon atoms inclusive.

For the deposition of the initial thin layer of pyrolytic graphite the inert gaseous diluent is mixed with the hydrocarbon gas in a volume to volume ratio ranging from about 3 parts of diluent to 1 part of hydrocarbon to about 20 parts of diluent to 1 part of hydrocarbon.

For the deposition of the final outer coating of pyrolytic graphite the volume ratio of diluent to hydrocarbon is preferably maintained from about 7 to 1 to about 20 to 1. Highly satisfactory results have been obtained by using a volume ratio of 10 parts of diluent per part of hydrocarbon during the deposition of the outer coating of pyrolytic graphite.

Relatively high ratios of diluent to hydrocarbon are generally preferred since these tend to produce less soot in the container, facilitate control over the thickness of the deposit and provide more efficient utilization of the hydrocarbon gas.

The initial deposit of pyrolytic graphite must be of sufficient thickness to prevent fusion of the radioactive particles during the high temperature deposition of the outer layer. Suitable initial layers can be from about 5 microns to about 50 microns or higher in thickness. Preferably the initial layer is from about 5 to about 20 microns thick.

The thickness of the final outer layer of pyrolytic graphite is not narrowly critical and will depend in large measure on the end use for which the coated radioactive substance is prepared.

As was previously mentioned, the temperature at which the initial layer of pyrolytic graphite is deposited must be lower than the surface sintering point of the radioactive particles. Therefore, the temperature of the initial deposition must be determined in view of the particular radioactive material to be coated. The outer layer of pyrolytic graphite is deposited at temperatures above the surface sintering point of the particulate radioactive material and, in any event, above 1800° C. The maximum obtainable deposited density in pyrolytic graphite is reached at about 220° C. In order to minimize any tendency toward migration of the uranium, deposition temperatures above 2200° C. are not recommended. The actual temperature at which the final coating is applied should be selected upon consideration of the temperatures to which the final product will be exposed.

The coefficient of thermal expansion of nuclear fuel materials are generally greater than the coefficient of thermal expansion of pyrolytic graphite. Because of this differential there are advantages to depositing the pyrolytic graphite at as high a temperature as possible within the aforesaid limitations. When the coated radioactive particle cools the particle shrinks within the graphite shell thus leaving a space for reexpansion upon any subsequent heating and therefore minimizing the danger of cracking the protective shell of pyrolytic graphite due to the internal stress caused by the expansion of the radioactive particle.

While the present invention is applicable to any radioactive metal or metal compound it is particularly applicable to coating radioactive metal carbides with pyrolytic graphite.

The figure is a photomicrograph showing a sectional view of a uranium carbide particle 1 coated with an inner layer of laminar pyrolytic graphite 2 and an outer layer of columnar pyrolytic graphite 3.

The following examples will further illustrate the present invention.

Example I

Fifty grams of uranium dicarbide particles having a sintering temperature of 1775° C. and ranging in size from 177 to 250 microns were heated in a fluidized bed furnace having an inside diameter of 1 inch. The particles were suspended by helium flowing at a rate of 4.3 liters per minute. When the temperature of the particles was between 1700° C. and 1750° C. methane was introduced at a rate of 1.2 liters per minute. These conditions of temperature and flow rate were maintained for 15 minutes after which the methane flow was shut off and the particles allowed to cool. The uranium carbide particles were found to have a coating of laminar pyrolytic graphite which was from 12 to 14 microns thick.

The coated particles were then removed from the furnace and washed in an 8 molar solution of nitric acid to eliminate impurities and surface contamination. Then 15 grams of the coated particles were replaced in the fluidized bed furnace and fluidized by helium flowing at the rate of 4.5 liters per minute. The particles were heated to 1800° C. at which point methane was introduced at the rate of 0.6 liter per minute. These conditions were maintained for a period of 1 hour and 45 minutes during which a layer of columnar pyrolytic graphite 60 to 80 microns thick was deposited.

Example II

Thirty grams of uranium dicarbide particles ranging in size from about 50 to about 100 microns and having a surface sintering temperature of about 1550° C. were heated in a fluidized bed furnace having an inside diameter of 1 inch. The particles were suspended by helium flowing at a rate of 3.5 liters per minute. When the temperature of the particles was between about 1450° C. and 1500° C. methane was introduced at a rate of 1.0 liter per minute. These conditions of temperature and flow rate were maintained for a period of about 20 minutes after which the methane flow was shut off and the particles allowed to cool. The particles were found to have a coating of laminar pyrolytic graphite which was approximately 10 microns thick.

The coated particles were washed in 8 molar nitric acid and then replaced in the furnace. The particles were fluidized by helium flowing at a rate of about 4.5 liters per minute and heated to about 1800° C., at which point methane was introduced at a rate of about 0.6 liter per minute. These conditions were maintained for a period of about 1 hour and 45 minutes during which period a layer of columnar pyrolytic graphite having a thickness of about 60 to 80 microns was deposited.

What is claimed is:

1. A radioactive particle having an inner uncracked coating of laminar pyrolytic graphite and an outer coating of columnar pyrolytic graphite, the interior volume enclosed by said inner coating being greater than the volume of the radioactive particle at all temperatures below the surface sintering temperature of the particle.

2. A product as in claim **1** wherein the radioactive particle is uranium carbide.

3. A product as in claim **1** wherein the radioactive particle is thorium carbide.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,306,825 Dated February 28, 1967

Inventor(s) Robert L. Finicle

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 57, "220°C" should read --2200°C--.

Signed and Sealed this

sixteenth Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks