United States Patent Office

3,554,783

Patented Jan. 12, 1971

3,554,783

LOW TEMPERATURE METHOD FOR COATING NUCLEAR FUELS WITH MULTIPLE CARBON COATINGS

Hans Beutler, Sulz-Attikon, Switzerland, assignor to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Filed Nov. 4, 1968, Ser. No. 773,351

Int. Cl. G21c *3/20*; B44d *1/16*

U.S. Cl. 117—46 2 Claims

ABSTRACT OF THE DISCLOSURE

A thin, impervious, carbon coating is deposited onto a porous buffer coating in pyrolytically coated fuel microspheres to prevent diffusion of the coating gas into the porous buffer coating during subsequent coating operations by initiating the deposition at a temperature of about 1500° C. and immediately thereafter reducing the deposition temperature to within the range of 1100°–1300° C. to complete deposition of an outer, high density pyrolytic carbon coating.

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of, or under, a contract with the U.S. Atomic Energy Commission. It relates generally to coated fuel particles and more particularly to an improved low temperature process for depositing multi-carbon coatings onto selected nuclear fuel microspheres.

In the extensive art generated in the coated fuel particle technology it has been found that in order to insure integrity of the fuel particle, multi-layers of coating material should be employed. One such coating configuration comprises a highly porous, low density carbon coating deposited about the fuel core followed by an outer impervious coating of high density pyrolytic carbon These coated fuel particles have been found to have minimal fuel failure caused by fission product recoil damage and rupture of the coating from thermal stresses and internal pressure build-up from fission product gases under irradiation. In a recent advance, described in U.S. Pat. 3,471,314, issued Oct. 7, 1969, in the names of Ronald L. Beatty and Dale B. Kiplinger for "Pyrolytic Carbon Coating Process," a low temperature deposition process was described for laying down this outer high density pyrolytic carbon coating which is isotropic. There a coating gas selected from propane, 1,3 butadiene, or propylene, was employed and the deposition conducted at a temperature between 1100°–1300° C. While this process offered distinct advantages over the earlier prior art high temperature processes, it was found that some diffusion of the coating gas into the highly porous, low density inner coating with subsequent carbonization occurred, thereby decreasing the void volume of the porous deposits and increasing their density. It is highly desirable and an object of this invention to provide a low temperature deposition process for depositing an outer, isotropic, pyrolytic carbon coating onto this highly porous, carbon coating without attendant decrease in void volume and increase in the inner porous coating density.

SUMMARY OF THE INVENTION

This object is achieved by initiating the deposition at a temperature of about 1500° C. and immediately thereafter reducing the temperature to a value within the range of 1100°–1300° C. to complete deposition of the outer high density, pyrolytic carbon coating. This short high temperature exposure, employing propane, 1,3 butadiene or propylene as the coating gas, was found to provide an effective diffusion barrier in the form of a thin, impermeable, carbon coating for the reactant gas and resulted in an insignificant increase in the density of the highly porous, low density inner carbon coating. Where the diffusion barrier was not deposited the highly porous, low density coating was found to increase from 0.8 to 1.2 grams/cc. Employing this modification to the low temperature deposition process resulted in a density increase of the highly porous, low density coating of from 0.8 to 0.85 grams/cc. Of importance also, was the fact that the density of the outer, high density, pyrolytic carbon coating was unaffected.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Inasmuch as the present invention is directed to a coating process the particular fuel core may comprise any of the well known fuels as discrete solid particles, such as thorium carbide, thorium oxide, uranium oxide, uranium carbide, uranium nitride, plutonium carbide, plutonium oxide, plutonium nitride, etc., and mixtures thereof. By the term "particle" it is intended to refer to spheroids of the selected fuel material prepared by any of the well known fuel processes, such as the sol-gel process, having an average particle diameter from 1–1000 microns, preferably from 250–500 microns.

As noted hereinbefore the present process relates to certain improvements in the prior art low temperature deposition process described in U.S. Pat. 3,471,314. In accordance with that process an inner, low density, highly porous carbon coating is first deposited about the fuel particles, such as spherical thoria sol-gel derived microspheres, employing undiluted acetylene as the coating and fluidizing gas at a deposition temperature of about 1050° C. The deposition is preferably carried out in a conventional fluidized bed reactor, the design of which is well known in the art. This coating, which will hereinafter be referred to as the "buffer" coating, may be of varying thickness but generally comprises a thickness of about 40 microns. When this thickness is built up helium gas is substituted for the acetylene to terminate this deposition phase while maintaining fluidization of the particles prior to further coating operations.

Previously the reactor temperature was then equilibrated to a value within the range of 1100°–1300° C. and a coating and fluidizing gas selected from propane, 1,3 butadiene, or propylene substituted for the helium to deposit a high density, isotropic, pyrolytic carbon coating. In accordance with the present invention the reactor temperature is raised to about 1500° C. to initiate deposition of the pyrolytic carbon coating. At this higher deposition temperature a thin, highly impermeable, carbon coating is rapidly deposited on the buffer coating, sealing the pores and precluding diffusion of the coating gas into the

buffer coating. This thin, impermeable, coating is deposited almost instantaneously and immediately thereafter the temperature of the reactor can be reduced to within the range of 1100°–1300° C. and the coating operation conducted in accordance with the low temperature process previously described to deposit the outer high density pyrolytic carbon coating. Only about five minutes are required to complete deposition of the outer pyrolytic carbon coating to a thickness of about 65 microns at a temperature of 1250° C. The thickness of this impermeable carbon coating is in the range 1–5 microns.

Having described the invention in a general fashion the following examples are given to indicate with greater particularity the process parameters and techniques.

Example I

A 25-gram batch of spherical sol-gel derived thoria microspheres (200–250 microns diameter) was placed in a fluidized bed reactor. The reactor comprised a vertical graphite tube having a conical bottom and a single-hole gas inlet in a graphite resistance furnace. In a first experiment the reactor was brought up to a temperature of 1050° C. using helium as the fluidizing gas at a supply rate of 4 l./min. Then undilute acetylene gas was substituted for the helium at a supply rate of 4 l./min. to deposit a low density, highly porous carbon buffer coating onto the thoria microspheres. This coating phase was continued for 1.5 minutes and resulted in a coating thickness of about 38 microns. A portion of the coated microspheres was analyzed and the density of the coating determined by burning the coating for weight loss determination and microradiographic measurements for volume determination.

In accordance with the prior art low temperature deposition process a portion of these coated thoria microspheres was coated in a second experiment with a high density, isotropic, pyrolytic carbon coating using propylene as the coating gas at a supply rate of 4 l./min. and at a temperature of 1250° C. This coating phase was continued for 5 minutes and resulted in a coating thickness of about 65 microns. The density of the outer pyrolytic carbon coating was determined by density gradient column. The results are given in the accompanying table.

Example II

A 25-gram batch of the low density, highly porous carbon coated thoria microspheres prepared in Example I was coated in a third experiment with a high density, isotropic, pyrolytic carbon coating in accordance with the present process. Microspheres having the buffer coatings were placed in the fluidized bed reactor described in Example I and fluidized with helium at a supply rate of 4 l./min. while the temperature of the reactor was raised to 1500° C. Then propylene gas at a supply rate of 4 l./min. was substituted for the helium to initiate deposition of the thin, impermeable, carbon coating. Immediately thereafter the reactor temperature was reduced to about 1250° C. and the deposition continued for a period of about 5 minutes. This resulted in a pyrolytic carbon coating of approximately 65 microns in thickness.

The coated microspheres were analyzed and density determinations made for the inner porous coating as well as the outer, high density, pyrolytic carbon coating. The

density of the porous coating was determined by calculation from total particle density and volumetric measurements from a microradiograph. The density of the outer pyrolytic carbon coating was determined by density gradient column. The results are given in the accompanying table.

TABLE I

	Deposition temp. (° C.)	Coating gas	Supply rate (cm.³/min./cm.²)	Coating density: Buffer coating (g./cm.³)	Coating density: Outer coating (g./cm.³)
Experiment:					
1	1,050	C_2H_2	4.3	0.8	----------
2	1,250	C_3H_6	2.8	1.20	1.98
3	1,250	C_3H_6	2.8	0.85	1.98

It may be seen that the density of the porous buffer coating increased from 0.8 to 1.2 g./cm.³ in the experiment which was performed according to the prior art low temperature deposition process. On the other hand, where the thin, impermeable carbon coating was first laid down prior to depositing the outer high density pyrolytic carbon coating the density of the porous buffer coating increased only from 0.8 to 0.85 g./cm.³. This significant increase in the density of the porous buffer coating was achieved without any effect upon the density of the outer, high density, pyrolytic carbon coating.

What is claimed is:

1. In a method for preparing nuclear fuel microspheres having multiple carbon coatings consisting of an inner, porous, buffer carbon coating and at least one layer of high density pyrolytic carbon as an outer coating wherein said outer coating is deposited by thermally decomposing a hydrocarbon gas selected from propane, 1,3 butadiene or propylene at a temperature within the range of 1100°–1300° C. the improvement comprising the steps of rapidly depositing a first layer of carbon onto said porous carbon coating at a temperature of about 1500° C. to thereby seal the pores of said porous carbon coating and thereafter reducing the deposition temperature to within said range of 1100°–1300° C. to deposit said outer high density pyrolytic carbon coating.

2. The method of claim **1** wherein said deposition at about 1500° C. is carried out for a time sufficient to deposit said first layer of carbon to a thickness of 1 to 5 microns.

References Cited

UNITED STATES PATENTS

3,151,037	9/1964	Johnson et al.	176—67
3,247,008	4/1966	Finicle	117—100X
3,298,921	1/1967	Bokros et al.	176—67
3,306,825	2/1967	Finicle	176—67
3,325,363	6/1967	Goeddel et al.	117—100X
3,471,314	10/1969	Beatty et al.	117—100X

WILLIAM D. MARTIN, Primary Examiner

M. R. P. PERRONE, JR., Assistant Examiner

U.S. Cl. X.R.

117—69, 100; 176—67, 91