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Release of Fission Products from Pyrocarbon-Coated HTGR Fuel Particles During Postirradiation Anneals

M. T. Morgan
H. J. de Nordwall
R. L. Towns

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OAK RIDGE NATIONAL LABORATORY

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RELEASE OF FISSION PRODUCTS FROM PYROCARBON-COATED
HTGR FUEL PARTICLES DURING POSTIRRADIATION ANNEALS

M. T. Morgan
H. J. de Nordwall*
R. L. Towns

*Present address: O.E.C.D. Dragon Project
Winfrith, England

DECEMBER 1974

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HTGR FUEL PARTICLES DURING POSTIRRADIATION ANNEALS

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ABSTRACT

This report contains the data, results, and evaluations of postirradiation annealing studies of coated HTGR fuel particles. The purpose of the studies was to compare the capability of various pyrocarbon coatings for retaining fission products, including strontium, barium, and cerium, but primarily cesium. Experimental methods for annealing and examining coated particles are discussed. Constant-potential diffusion equations were used to calculate diffusion coefficients and the concentrations in the outer coating at the buffer-to-outer-coating interface. The results revealed kernel trapping effects and have indicated the possibility of a cesium concentration limit of $\sim 2 \times 10^{19}$ atoms/cm³ in low-temperature-deposited isotropic pyrocarbon coatings of high density. Diffusion coefficients for cesium in the low-temperature-deposited isotropic pyrocarbon coatings were found to be an order of magnitude higher than in high-temperature-deposited isotropic pyrocarbon coatings. The diffusion coefficients obtained will be useful in determining the maximum cesium release from similar coated particle fuel during irradiation. Data concerning a trapped fraction and a concentration limit can direct further research which might provide more accurate estimations of cesium release from coated particles during irradiation.

1. INTRODUCTION

This report summarizes a series of experiments, performed at ORNL during the period 1967-74, which were aimed at defining the retention of fission products that can be expected from the pyrocarbon-coated fuel particles used as fuel in HTGRs. Emphasis is upon making the large collection of data from these experiments generally available in a useful form. Companion publications^{1,2} review the mathematical representations of the release processes studied in laboratory experiments and the

application of laboratory results to the prediction of fission product release in reactors.

The models and coefficients generated during this work are being used to produce fission product source terms for computer codes that describe the release of metallic fission products from HTGR cores.^{3,4} These codes are applied to two classes of practical problems. The first is the calculation of primary circuit inventories resulting from normal operation to obtain source terms for design basis accidents,⁵ gamma-radiation intensities arising from deposited cesium and other fission products, and the concentrations of gas-borne fission products in the coolant that determine leakage through the PCRV. The second type of problem comprises analyses of the consequences of accidents in which all or part of the core is heated to abnormally high temperatures.^{5,6}

Two types of particles, fissile and fertile (see Fig. 1.1), are used in HTGR fuel elements developed in the United States. The fissile particles contain enriched uranium (93% ^{235}U), or ^{233}U bred in prior cycles, and thorium, if specified. The fissile particles have TRISO coatings, which consist of a SiC layer sandwiched between two low-temperature isotropic (LTI) pyrocarbon coats. The fertile particles, which contain only thorium, have BISO coatings that include two LTI coats but no SiC layer. Each type of particle has an initial coating of very-low-density pyrocarbon. This buffer coating absorbs the energy from fission recoil and provides void volume for expansion and gas collection.

These particles may be assembled into rigid shapes by a variety of matrix intrusion, extrusion, and molding processes. The resulting fuel rods or components, whose fuel loadings and matrix densities may differ considerably, are then loaded into graphite sleeves, blocks, or shells to form fuel elements.⁷ The factors relating to fission product control that influence the choice of fuel element type are the average thermal conductivity, which determines the peak temperature, and the variations in fuel particle and fuel rod construction, which determine the frequency of coating fracture during production and in service.

To ensure that a range of different fuel types could be examined conveniently and at moderate cost, most workers have performed their

PHOTO 96159

COATED PARTICLES

Fig. 1.1. Fissile and fertile coated fuel particles. (Photograph supplied through the courtesy of the General Atomic Company)

initial experiments using particles in which the fission product generation and release steps are separated in time. We are no exception.

It is recognized that some parameters that control fission product release may be affected significantly by irradiation so that releases measured in the absence of fission may be different. Coating properties are also known to change with exposure to energetic neutrons. Confirmation in-reactor is being sought as fuels irradiated at known temperatures become available from the HTGR fuel development program. Confirmation of fractional releases below 20% necessitates special capsule irradiations in which particles of a given specification are isolated, since it is impractical to determine releases of this magnitude by measuring fission product recovery in the particle.

A second limitation in the current data set is that it does not include results for reference BISO-coated ThO_2 particles made in a production coater because such fuels were not available. The use of generic property data is satisfactory if the typically larger uncertainties are acceptable. In the event that this is not the case, specific fuel qualification experiments will be needed for production coatings. This report includes release data for five different BISO fuel types. Results are given in tabular form along with derived coefficients, when possible.

Early experiments, which took the form of scoping tests of the products of various vendors who often did not disclose the structural characteristics of their products, even when they were known, revealed the following description of fission product behavior in coated particles:

- (1) Pyrocarbon coatings retain krypton, xenon, iodine, and tellurium up to 2000°C.
- (2) Pyrocarbon coatings are slightly permeable to cesium and cerium above 1000°C and practically transparent to strontium and barium. For this reason, some designers favor the addition of layers of silicon carbide or other very impermeable materials to the coating. An explanation for the migration of the solid fission products in pyrocarbon while gases are retained may be similar to that given by Evans et al.⁸ for the diffusion of actinides in pyrocarbon; that is, mobility

is gained by a reduction in size of the diffusing species associated with ionization. The degree of ionization depends both on the ability of the lattice structure to accept electrons and the strength of the forces holding them to the diffusing atoms. Thus noble gases are reluctant to share electrons and become immobile; and SiC, which does not easily accept electrons, is impermeable to most of the fission products.

- (3) Other metallic fission products are retained by the fuel kernel at HTGR operating temperatures.

Of the many metallic fission products, cesium and strontium represent the greatest potential nuisance and radiological hazard. Both have long half-lives and are relatively mobile in an HTGR. Cesium isotopes emit several hard gamma-rays, whereas strontium has a high affinity for animal bone.

Oxide kernels have been found to control the release of uranium and strontium,⁹ as well as cerium and other rare earths,¹⁰ better than carbides. The migration of uranium in pyrocarbon coatings on oxide and carbide particles during irradiation at 1400°C is discussed in ref. (11). Reviews of early work may be found in the reports of T. G. Godfrey et al.,¹² de Nordwall and Sayers,¹³ and Baumann and Reagan.¹⁴

The work reported in the succeeding sections describes a continuing attempt to improve our understanding and quantification of the release process for important fission products.

2. EXPERIMENTAL PROCEDURE AND APPARATUS

2.1 Experimental Procedure

The diffusion coefficient characteristic of transport in the coating was selected initially as the parameter most likely to determine cesium release from a pyrocarbon-coated particle, although it was recognized that this may not hold for all elements. The experimental procedure involved measuring the time required for cesium to penetrate the coating during an anneal at constant temperature. Diffusion coefficients and driving potentials were calculated using the delay time, the slope of the release curves, and the constant-potential equations described below.

2.1.1 Methods of calculating release parameters

Fission products are generated in the kernel by irradiating the fuel at temperatures below 800°C, where only small amounts of fission products recoil into the buffer layer and diffusion of fission products into the outer coating is negligible. The even smaller fraction generated from uranium contamination in the coating is neglected. This situation corresponds to the boundary condition that the initial concentration in the outer coating is zero. At a higher annealing temperature, fission products begin to move into the dense outer coating and out of the kernel. Since no means of determining whether the release is governed by a constant or depleting potential is available a priori, all data were analyzed with reference to constant-potential conditions because this was more likely to represent the technically important case of a high-burnup fuel. The constant-potential diffusion equation¹⁵ and derivations of relations (given below) which were obtained from it are discussed in Appendix A.

The concentration in the outer coating, $C_2(a)$, at the buffer-to-outer coating interface (radius a) may be obtained by the use of the release data and the equation

$$C_2(a) = \frac{3mM_1^0 t_0}{2\pi ab\ell} \quad , \quad (1)$$

where

- m = slope of the release curve, $(\text{sec})^{-1}$,
- M_1^0 = initial inventory of cesium, atoms,
- a = radius at the buffer-to-outer coating interface, cm,
- b = radius of the outer coating, cm,
- ℓ = thickness of the outer coating = $b - a$, cm,
- t_0 = intercept of the linear portion of the curve showing the release, FR, vs time, T , at $FR = 0$.

The apparent diffusion coefficients, D^* , were used for comparison of the fission product retention by different coatings. These coefficients were obtained by assuming that a constant potential existed and by using the relation

$$D^* = \ell^2/6t_0 \quad . \quad (2)$$

The use of this relation to obtain the true diffusion coefficient, D , when diffusion under conditions of a depleting potential is in effect will cause an error of not more than a factor of 3 (see Appendix A).

Release-vs-time plots of constant-potential diffusion data are commonly presented in the literature in the dimensionless form

$$N(t)/VC_2(a) \text{ vs } Dt/\ell^2 ,$$

where

$N(t)$ = the amount released at time t ,

V = $4\pi a b \ell$,

D = diffusion coefficient.

It is shown in Appendix A that

$$N(t)/VC_2(a) = FR/6t_0^m , \quad (3)$$

and

$$Dt/\ell^2 = t/6t_0 , \quad (4)$$

where

FR = $N(t)/M_1^0$,

M_1^0 = total amount of cesium at $t = 0$,

m = slope of the release curve.

The dimensionless form is a convenient way of plotting data with widely differing intercepts and slopes, and is used in this report to compare experimental data with solutions to the constant-potential equation. When a constant potential can no longer be maintained, due to depletion of the source, the experimental release curve will fall below that calculated for a constant driving potential. One practically important result of changing to a depleting source situation is that additional parameters are required to describe the process; it is then necessary to include the variable source concentration, $C_1(t)$, and the partition coefficient, ϕ , as well as the apparent diffusion coefficient, D^* .

2.1.2 Coated-particle operations and annealing

Following irradiation, the coated particles were examined under a microscope to eliminate visibly defective coated particles; then, contact radiographs were made of many of the coated particles to determine the

kernel and coating dimensions.¹⁶ Single coated particles were used in order to associate the cesium release during the anneals with the dimensions of the individual particle. Some of these particles were obtained from irradiated bonded fuel pellets by disintegrating the matrix and separating the coated particles; however, most of them had been irradiated in a loose bed. Before annealing, the coated particles were analyzed for total fission product content. They were subsequently loaded into individual tungsten tubes and annealed in an eight-tube crucible in an induction furnace at temperatures between 1250 and 1600°C. In some cases, groups of particles or bonded fuel pellets of coated particles were used. These were annealed at 1150°C or 1250°C in a resistance furnace. All the samples were annealed in a series of steps, at the temperature selected for the series, in order to determine the cesium release as a function of time. The helium sweep gas passing over the samples was continuously monitored with a Geiger tube to detect any ^{85}Kr release which would indicate coating failure. The furnace was turned off after each step, the coated particles were removed, and the coated particles and the furnace components were analyzed using a gamma-ray spectrometer. In a few cases, some of the coated particles were mounted, sectioned, and polished for ceramographic examination.

2.2 Apparatus and Handling Techniques

2.2.1 Equipment for handling coated particles

The unloading of inner capsules from irradiation experiments and the handling of coated particle samples and bonded fuel pellets are performed in a shielded glove box (Fig. 2.1). (Bench-top operations using a tray and a plastic shield have been utilized for transfer and examination of single coated particles.) The glove box is shielded with 4 in. of lead, which is sufficient to shield a fuel sample activity of 8 Ci (38 days' decay). Special features of the glove box include wrist-action manipulators, a shielded storage facility in a well at the bottom of the box, a 30-power periscope, a remotely controlled revolving stage for the periscope, a shielded Geiger tube probe to find lost particles, and a suction particle pickup controlled by a foot switch. This equipment and the techniques for handling and annealing the coated particles have been described elsewhere.^{17,18}

PHOTO 91518

Fig. 2.1. Shielded glove box.

2.2.2 The induction furnace and gas handling system

The high-temperature annealing furnace is located in a shielded glove box identical to the one described in Sect. 2.2.1. The flow diagram for the system is shown in Fig. 2.2. Purified helium sweep gas passes over the sample at a flow rate of 100 cc (STP)/min and a pressure of about 100 torr, carrying any released fission gases through a filter and into an enclosed vacuum system for counting and collection. As a means of detecting coating failures, the fission gas is continuously monitored for ^{85}Kr as it flows through a coaxial Geiger-Mueller tube and is collected on a molecular sieve trap at liquid nitrogen temperatures. This gas can be pumped out of the trap by the Toepler pump into a total gas counting system for a more sensitive analysis, or into bulbs for analysis elsewhere.

In an earlier procedure, samples were placed in a graphite crucible for annealing and the graphite crucible was heated by induced current supplied by a 10-kW output rf generator. Later, the graphite crucible was modified to accommodate eight tungsten tubes in a symmetrical arrangement, as shown in Figs. 2.3 and 2.4. The crucible was drilled vertically to accommodate eight 1/16-in.-OD tungsten tubes. The holes in the graphite crucible were 1/2 in. deep, and a center hole 1/8 in. in diameter by 1/2 in. deep was provided so that the temperature could be measured with an optical pyrometer. Each tungsten tube was fitted with a pyrocarbon thimble (capacity, one coated particle) to prevent the coated particle from touching the tungsten wall. The crucible is supported on tantalum wires inserted into alumina tubes.

Short stainless steel guide wires which are attached to a stainless steel position ring at the top of the crucible assembly slide into the tungsten tubes to hold them in position. This type of arrangement was needed since the assembly is tilted 45° to face the window of the shielded box. The guide wires are of different lengths, ranging from 3/16 to 5/8 in., in order to facilitate their placement in the tungsten tubes with tongs.

The temperature of the furnace is controlled by a signal from a radiation pyrometer during isothermal anneals. The temperature is determined with an optical pyrometer which has been calibrated for the absorption of the lead-glass window. The system controls the temperature

Fig. 2.2. Flow diagram of annealing system.

Fig. 2.3. Induction-furnace tube assembly.

PHOTO 1876-74

Fig. 2.4. Multitube crucible.

to within 10°C of the set value over the range 1250 to 2000°C. The temperatures measured by the optical pyrometer were calculated to be within $\pm 30^\circ\text{C}$, which was judged to correspond to the uncertainty of measurements and calibrations using a standard lamp and the melting points of copper, platinum, and nickel.

2.2.3 The resistance furnace

A rhodium-wound resistance furnace illustrated in Fig. 2.5 was used for annealing samples at temperatures of 1250°C and below. The high-density alumina tube was used as the containment vessel to exclude air and to contain the helium sweep gas and the fission-product gases. After several hundred hours at 1250°C, the alumina tubes began to leak and had to be replaced. Although alumina is impervious to the gases, cesium diffuses through it; therefore, a tantalum liner was used to contain the metallic fission products. The gas system was similar to that of the induction furnace except that the Toepler pump transfer system was omitted. The flow rate of the helium sweep gas was 110 cc (STP)/min at a pressure of approximately 10 torr. When the collected gas was to be analyzed, the traps were transferred to the induction furnace gas collection system and pumped out.

2.2.4 Special operations

The coated particles were often deliberately cracked at the end of the annealing operation to confirm that the coating was still gas-tight, to separate the kernels and coatings for fission-product distribution studies, and to simulate coating failures in postirradiation annealing studies. To permit collection of gaseous fission products, the coated particles were cracked in a cylinder by a rod sealed with O-rings. The anvil contained a well which limited the travel of the rod to prevent the kernel from being crushed. The gas that was released was collected on a molecular sieve trap at liquid nitrogen temperatures using helium as a carrier. A micrometer screw-driven apparatus was used to obtain minimum fragmentation when gas collection was unnecessary.¹⁷

A limited number of coated particles were sectioned and polished for photomicrographic examination after irradiation and annealing. Because only a few particles were available, the usual technique of mounting a

Fig. 2.5. Resistance furnace annealing system.

large sample of particles could not be used. In our procedure, each coated particle was mounted separately with epoxy resin on a special block, the thickness of which was already known. (The diameter of the coated particle had also been measured previously.) The overcoat of epoxy resin was faced off to the upper surface of the coated particle on a lathe. The coated particle was then ground to midplane and polished on metallographic grinding and polishing equipment. When the coatings were opened during grinding, the voids in the coated particles were filled with epoxy resin by vacuum impregnation to fix the kernel. Other details of preparation and photography have been described elsewhere.¹⁹

2.2.5 Disintegration of bonded fuel rods containing coated particles

Many methods were tested to determine their usefulness in disintegrating bonded fuel rods to obtain samples of the coated particles for analysis or annealing experiments, to determine fission-product distribution in the fuel rods, or to determine the number of coating failures.²⁰ The only practical method which disintegrated the fuel pellets or rods in a reasonable time without cracking or altering the particle coatings significantly was an electrolytic technique described by Koss and Bildstein.²¹ However, it left considerable amounts of matrix clinging to the separated coated particles. We found that immersing the reaction vessel in an ultrasonic bath during the disintegration process would remove most of this debris. During initial trials, fuel rods 1/2 in. in diameter by 2 in. long were disintegrated in 2 to 14 hr using currents of 1 to 2-1/2 A and nitric acid concentrations of 1 to 2-1/2 M. We found evidence that this treatment caused spalling on the surfaces of some of the coated particles. Decreasing the acid concentration increased the time required to disintegrate the fuel rods and increased the spalling. The conditions determined to be most suitable for irradiated fuel rods were a current of 2 A and a nitric acid concentration of 2-1/2 M.

One method which might have an application in fuel recovery is the immersion of fuel rods in liquid sodium-potassium alloy (NaK) at room temperature. In this method, both the matrix and the coatings were rapidly disintegrated, leaving only the kernels intact. The alkali metal was removed by reaction with butyl alcohol. Unfortunately, the tendency of

NaK to ignite on contact with air and the formation of hydrogen during reaction with the alcohol make this procedure extremely hazardous.

2.3 Collection and Analyses of Fission Products

2.3.1 Collection of fission products

When graphite crucibles were used in the induction furnace system without tungsten tubes, fission products were found to collect on the crucibles and on replaceable quartz sleeves which line the furnace tube. Analyses showed that more than 99% of most of the solid fission products released from the fuel particles were retained in the crucible and on the quartz liners at sample temperatures up to 2000°C. Cesium is collected quantitatively on the quartz liners. When tungsten tubes were used, the cesium was deposited over a 3-in. length inside the tubes as shown in Fig. 2.6; only a small fraction of the total amount released was retained on the carbon thimbles. The latter accumulation was minimized by changing the thimbles during the annealing series. The thimbles were also replaced frequently to prevent the tungsten from diffusing through into the coated particles. During the annealing series, components were analyzed periodically to obtain stepwise functions of fission product release vs time. Occasionally, it was necessary to replace some components in order to reduce interference between isotopes during analyses.

The cesium was deposited over a longer length on the cooler sections of the tantalum liner in the resistance furnace system. Most of it was found downstream just below the near-isothermal hot section at temperatures ranging between 0 and 1000°C, as shown in Fig. 2.5. A small amount was collected upstream of the hot zone; only a negligible amount was collected in the ceramic wool filters at the ends of the furnace tube.

2.3.2 Fission product analyses

Nondestructive gamma-ray analyses were performed to determine ^{89}Sr , ^{91}Sr , ^{95}Zr , ^{95}Nb , ^{103}Ru , ^{106}Ru , ^{131}I , ^{132}Te , ^{134}Cs , ^{137}Cs , ^{140}Ba , ^{140}La , ^{141}Ce , and ^{144}Ce . Very few experiments were performed early enough after irradiation to allow the shorter-lived isotopes to be found. Only ^{90}Sr , ^{106}Ru , ^{134}Cs , ^{137}Cs , and ^{144}Ce remained in most of the experiments. A

ORNL - DWG 74-7236

Fig. 2.6. Cesium distribution on tungsten tube.

multichannel analyzer was used for the gamma-ray analyses. A sodium iodide detector was necessary for identifying the small amounts of fission product activity collected on the furnace components, while a lithium-drifted germanium detector was used to resolve the higher and more complex fission product activities in the coated particles.

2.4 Sources of Error in Experimental Measurements and Calculations

2.4.1 Possible errors in measurements

Measurements of annealing time, temperature, fission product activity, and coated particle dimensions were made in these experiments. The measurement of annealing time in the induction furnace is considered accurate to ± 2 min. Approximately 1-1/2 min was required to bring the crucible to within 30°C of the set temperature at which the timing for the anneal was begun, and up to 1 min was required to set the temperature exactly. Timing of anneals in the resistance furnace was less accurate, probably about ± 20 min. This furnace took about 1-1/2 hr to reach temperature; and timing was begun, as with the induction furnace, when the temperature was within 30°C of the set temperature. The absolute temperatures of both furnaces were believed to be accurate within $\pm 30^\circ\text{C}$; the constancy of temperature during a given anneal was better than $\pm 10^\circ\text{C}$.

The accuracy of fission product activities determined by gamma-ray spectroscopy was dependent on the count rate, the counting time, the dimensions of the sample, and the background due to mixtures of fission products. Coated fuel particles were ideal as point sources of activity, but the complex fission product mixtures present, especially during the period shortly after irradiation, made resolution of the spectra with the sodium iodide detector impossible without the use of special computer techniques and caused considerable error in the determination of cesium using the lithium-drifted germanium detector. Measurements of cesium on coated particle samples were generally reproducible within 20% about two months after irradiation and within 5% a year or more after irradiation. The fission products collected on the furnace components were a less complex mixture, usually consisting only of ^{89}Sr , ^{90}Sr , ^{134}Cs , ^{137}Cs , ^{141}Ce , and ^{144}Ce . Collections soon after irradiation also included ^{140}Ba . Calibrations were made for absorption and for the shapes and

sizes of the various components. The accuracy of fission product analyses on crucibles, thimbles, and tungsten tubes was within $\pm 5\%$ as long as the activity level was sufficiently high to allow placement of these components at such distances from the detector that geometrical errors were reduced. The determinations on larger furnace components were considered less accurate, generally within $\pm 10\%$. A method of rotating tubular components during analysis was developed to minimize the effects of uneven distributions of fission products.

Measurements of coated particle dimensions were taken from micro-radiographs using a microscope with a Fowler eyepiece; a few were made from photomicrographs. A discussion of possible errors in these measurements is given by Hewette et al.²² Most of the dimensions taken from microradiographs were readable within $\pm 2 \mu\text{m}$. Some of the contours at the buffer-to-outer-coating interface were barely visible; however, repeated measurements of these dimensions were reproducible within $\pm 4 \mu\text{m}$.

2.4.2 Possible errors involved in the use of the constant-potential equations

The assumptions made in our study in order to justify the use of the constant-potential relation were as follows:

1. A constant potential exists long enough for a constant release rate to be determined.
2. The concentration at the outer boundary is zero at all times.
3. The concentration in the outer coating is zero at the start of the annealing series.

We have presented some evidence in Sect. 5.2 that the first assumption existed for some anneals but not for others. In the absence of this condition, that is, for the case of a depleting potential, it can be shown (see Appendix A) that the D calculated will be high by as much as a factor of 3 and that the concentration $C_2(a)$ calculated will be low, representing some average value less than $C_2(a, +0)$, where $C_2(a, +0)$ is the initial concentration in a depleting system. Of course, if the anneal is carried to complete depletion, the curve can be analyzed to obtain correct values.

The best evidence in support of the second assumption for cesium release is that the cesium retained on the matrix and graphite cans of fuel pellets during the 1250°C anneals was insignificant and that

distribution data for the furnace tubes (Figs. 2.5 and 2.6) show little or no cesium in the high-temperature zones. No detectable cesium was collected when coated particles were washed in acid after being annealed at 1400°C; therefore, the existence of a film is not likely.

While film or evaporation effects are probably unimportant for cesium at the temperatures and release rates involved at the surface of the coated particles, some of the coated particles investigated (viz., Group A) were overcoated with a sacrificial layer which might produce an apparent film effect. Film or evaporation coefficients are discussed in ref. 1 and Appendix A. The result of any film effect would be to lower the calculated value of D; however, the diffusion coefficients calculated for Group A coated particles are already higher than those of other groups. These complications with the Group A coated particles can be eliminated by grinding the sacrificial layers off the coated particles before annealing.

The third assumption depends on the irradiation temperature and time. All irradiation temperatures in these experiments were reported to be below 800°C, although the HFIR irradiation (Groups C, F, G, and H) was not instrumented.

3. CHARACTERIZATION AND HISTORY OF MATERIALS USED

3.1 Characterization Procedures for Pyrocarbon Coatings

Density, anisotropy, and crystallite size have been used to characterize pyrocarbon coatings in the past. It was formerly anticipated that these coating properties might be correlated with fission product release and coating stability to give quality control indexes. However, there is considerable doubt as to the precision of the measurement of these properties; in addition, it is now believed that the amorphous-to-crystalline carbon ratio and microstructural details not fully reflected by these properties may have equal, or greater, effect on both fission product release and coating stability. Until an effective, complete characterization procedure becomes available, the pyrocarbon coatings may be studied relative to the manufacturing process (i.e., in this case classified as LTI or HTI pyrocarbon, where LTI and HTI refer to low-temperature and high-temperature deposition of isotropic pyrocarbon respectively.)

Densities of the coatings are determined, in part, by sink-float or density gradient column techniques.²³ It has recently been discovered that large errors may occur even in coatings with measured high densities due to penetration of the liquids used into open surface porosity.²⁴ The crystallite sizes and Bacon anisotropy factors (BAF)²⁵ are determined by x-ray diffraction studies. Currently, the degree of orientation or anisotropy is also determined optically (OPTAF);²⁶ however, the OPTAF determinations have not been perfected to provide reliable results.²⁷ The more reliable x-ray diffraction studies are performed on disk samples, coated simultaneously with the coated particles, but there is some doubt that the pyrocarbon deposited on the disks exactly duplicates the structure of that deposited on the particles. The x-ray diffraction studies are not adaptable to small samples of coated particles.

Other difficulties in the application of coating properties to fission product release studies are the result of changes in the coating properties due to fast neutron damage during irradiation. Routine pre-irradiation measurements of coating properties are made as part of quality control procedures, but postirradiation determinations are rarely performed because remotely controlled procedures are not yet available for such radioactive samples of limited size. Density changes in the coatings of some of the particles used were determined by averaging results calculated from dimensional changes of coated particles and those obtained by density gradient column measurements of pyrocarbon strips from disks coated with the particles and irradiated in the same capsule.^{28,29} These results are discussed in Appendix C.

Procedures for the determinations of microstructural detail and the amorphous-to-crystalline carbon ratio are being developed. Scanning electron microscope and transmission electron microscope studies of LTI pyrocarbon deposited from propane or propene, and HTI pyrocarbon deposited from methane, have been made at ORNL³⁰ and at the General Atomic Company.³¹ These studies show distinct differences between LTI and HTI pyrocarbons of the same density. The LTI pyrocarbon has growth features which are smaller and appear more circular in shape, and the outer regions of the growth features appear less dense than the inner regions; therefore, these regions may contain a finer, more uniformly distributed porosity.

The results of these studies on structures may be applied to aid in evaluating other properties and explaining irradiation damage. Studies more applicable to quantitative determinations have included determination of the amorphous carbon distribution in coatings by examination of a prepared surface after oxidation,³² and determination of the amorphous-to-crystalline carbon ratio by an ultrasonic technique³³ or by a method depending on the difference between BAF and OPTAF determinations.³⁴

Indications of correlations of fission product and heavy metal diffusion with coating properties have been noted in related work. The release of barium was lowered by one order of magnitude as the coating density was increased from ~ 1.5 to 2.0 g/cm^3 .³⁵ Diffusion coefficients for actinides in pyrocarbon were reported by Evans et al.³⁶ to be three orders of magnitude greater in a direction parallel to the deposition surfaces than those in the perpendicular direction. A discussion of the role of preferred orientation of crystallites in diffusion is also given by Carlsen³⁷ and Chinaglia.³⁸

3.2 Properties of Coated Particles Used in the Annealing Experiments

Characteristics of the coated particles used are given in Table 3.1. Additional information and coating deposition conditions are presented in Appendix C. The outer coating densities (Table 3.1) are considered to be reasonable postirradiation values applicable for evaluation of the annealing experiments; however, the densities of coatings of Groups A, B, D, and E are preirradiation measurements which should not have changed significantly during irradiation. The densities of coatings of Groups C, F, G, and H were calculated from preirradiation values according to a formula derived from postirradiation measurements of coated particles and carbon strips irradiated with the coated particles as discussed in Appendix C. The anisotropies and crystallite sizes are preirradiation data. Some of these values were not available. Postirradiation measurements of these parameters were not determined.

3.3 Bonded Fuel Pellets

The Group A samples used in the annealing experiments included coated particles in loose beds and small bonded fuel pellets of coated particles

Table 3.1. Characteristics^a of coated particles

Group	Outer coating density ^b (g/cm ³)	Anisotropy ^c	Crystallite size ^c (Å)	Coating type	Fuel material
A	2.01	-	-	LTI	UO ₂
B	1.85	1.00	-	LTI	UO ₂
C	2.05	1	30	LTI	ThO ₂
D	1.83	1.06	-	LTI	UC ₂
E	1.82	1.00	-	HTI	UC ₂
F	1.95	1.1	110	HTI	ThO ₂
G	2.05	1.3	120	HTI	ThO ₂
H	2.07	1	120	HTI	ThO ₂

^aSee Appendix C for limitations and description of measurements and coating deposition conditions.

^bThese postirradiation values were calculated from preirradiation densities.

^cPreirradiation values.

irradiated in both the B9-41 and the B9-42 irradiation capsules. The fuel pellets were irradiated and annealed in graphite cans. Dimensions of the fuel pellets and the graphite cans are given in Fig. 2.5. Average surface areas of the pellets and graphite cans as determined by the BET method were 2.9 ± 0.06 and $0.098 \pm 0.05 \text{ m}^2$, respectively; the average weights of the pellets and cans were 0.395 ± 0.003 and $0.882 \pm 0.02 \text{ g}$, respectively. ThO_2 particles coated with diluent pyrolytic carbon were loaded along with the pyrocarbon (PyC)-coated UO_2 particles in a weight ratio of 25:1 in the fuel pellets and also in the loose beds of coated particles.³⁹ Each fuel pellet contained approximately 80 PyC-coated UO_2 particles.

3.4 Irradiation Data

The coated particles used in the annealing experiments were obtained from four separate irradiations. Table 3.2 lists the irradiation experiment, the reactor, the core position, the coated-particle groups contained in the irradiation experiments, the burnups, and the fast neutron fluences. Other details of the irradiations are given in Appendix C and refs. 40-42. Fission gas release data and results of postirradiation examinations of the Group A coated particles are given in ref. 40, that of Groups B, D, and E in ref. 43, and that for Groups C, F, G, and H in ref. 29, 44-46.

3.5 Ceramographic Examination of Coated Particles

Because of the expense and time involved in the preparation of sections of single coated particles as required on the limited postirradiation samples, only a few of the coated particles from selected groups were examined by ceramographic techniques. The photomicrographs of the postirradiation samples are compared with those of preirradiation samples from Groups A, C, and F coated particles below.

3.5.1 Group A coated particles

Figure 3.1 shows photomicrographs of Group A coated particles as-coated and after irradiation and annealing. Irradiation and annealing caused no apparent change in the coating structures. Fission gas voids are evident in the kernels of particles irradiated to 11% FIMA; in the particles irradiated to 22% FIMA, the voids have coalesced to form larger,

Table 3.2. A summary of irradiation data

Irradiation experiment	Reactor	Core position	Coated particle groups	Burnup (% FIMA)	Fast neutron fluence, E > 0.18 MeV (neutrons/cm ²)
B9-41	ORR	B-9	A	22	Low
B9-42	ORR	B-9	A	11	Low
C1-28	ORR	C-1	B, D, E	13	Low
HT-1	HFIR	F-7	C, F, G, H	3.5	4×10^{21}

AS COATED

AS IRRADIATED - 11 % FIMA

IRRADIATED TO 11 % FIMA AND
ANNEALED 156 hr AT 1400 °C

AS IRRADIATED - 22 % FIMA

IRRADIATED TO 22 % FIMA AND
ANNEALED 156 hr AT 1400 °C

IRRADIATED TO 22 % FIMA AND
ANNEALED 2500 hr AT 1250 °C

Fig. 3.1. Photomicrographs of Group A particles (LTI-PyC-coated UO_2).

less numerous voids. Annealing of the 11% FIMA and 22% FIMA particles at 1400°C for 156 hr, or the 22% FIMA particles at 1250°C for 2500 hr, produced no apparent change in kernel structure. The densification of the buffer layer at the kernel-to-buffer interface in the irradiated and annealed coated particles is due to fission fragment damage.

3.5.2 Groups C and F coated particles

Figure 3.2 allows a comparison of preirradiation photomicrographs with those taken after irradiation and annealing of Group C and Group F coated particles. Postirradiation photomicrographs were prepared from two out of four annealed coated particles available from each group. The kernels dropped out of two of the coated particles during preparation (one from each group), leaving these as the only complete photomicrographs. Preirradiation photomicrographs were limited.

No gross change is visible in the outer coating structure as a result of irradiation and annealing, but an apparent porosity is evident in both preirradiation and postirradiation photomicrographs of Group C outer coatings. This is in contrast with density measurements which showed that Group C coated particle coatings had the highest density, but this anomaly has been observed before⁴⁷ and can be explained if we consider that the apparent pores are pockets of low-density amorphous carbon or holes left where this material pulled out during polishing.

Porosity is also evident in the kernel of the irradiated, annealed Group C coated particle. The Group C and Group F coated particles were irradiated in the same capsule to the same burnup and were annealed simultaneously in the multitube crucible. Also, both groups had 275- μm -diam sol-gel ThO_2 kernels. The presence of postirradiation porosity in the Group C kernel, while none is evident in the Group F kernel, is at present unexplainable.

4. EXPERIMENTAL RESULTS

This section gives the results of early quality control experiments and presents samples of fission product release curves and a condensation of measured and calculated parameters from later, more specific, diffusion annealing studies. Tables of raw fission product release data from the

LTI - PyC COATED ThO_2 PARTICLE,
GROUP C, AS COATED

LTI - PyC COATED ThO_2 PARTICLE,
GROUP C, IRRADIATED TO 3.5% FIMA
AND ANNEALED 3700 hr AT 1400 °C

HTI-PyC COATED ThO_2 PARTICLE,
GROUP F, AS COATED

HTI - PyC COATED ThO_2 PARTICLE
GROUP F, IRRADIATED TO 3.5% FIMA
AND ANNEALED 3700 hr AT 1400 °C

Fig. 3.2. Photomicrographs of Group C (LTI-PyC-coated ThO_2) and Group F (HTI-PyC-coated ThO_2) particles.

later studies are presented in Appendix B.

4.1 Results of Early Experiments

In our early experiments, we simply tested current coated particle designs for stability and qualitative fission product release. Structural characteristics of the coated particles were not known quantitatively, in many cases not at all, and the irradiation temperatures were high, making initial and boundary conditions for postirradiation anneals unknown. Since irradiations were performed primarily to determine coating stability, materials available for fission product release studies were not suitable for basic studies in diffusion. The results of these qualitative annealing experiments at temperatures ranging from 1300 to 2000°C provided the information given below.

Of the major fission products (i.e., those having a significant yield and half-life), niobium, ruthenium, and zirconium are fixed in oxide or carbide fuel kernels. Cerium and yttrium, while fixed in oxide fuels, are released from the carbides.¹⁰ Iodine, tellurium, krypton, and xenon are effectively retained by pyrocarbon coatings while cesium, cerium, yttrium, strontium, and barium diffuse through the coatings at rates increasing in that order. No analyses were performed to determine tritium release.

Baumann and Reagan¹⁴ confirmed that PyC coatings were efficient containers for krypton, xenon, and iodine during irradiation at temperatures below 1600°C. Any release of these elements below 1600°C was found to result from fuel contamination in the coatings. Above 1600°C, some evidence of migration through the coatings was apparent.

In related work, oxide kernels were found to control the migration of uranium in pyrocarbon coatings better than carbides.^{9,11}

4.2 Experimental Results on the Release of Cesium

4.2.1 Typical graphs of cesium release vs annealing time

Typical graphs of cesium release vs time are shown in Figs. 4.1(a), 4.2(a), and 4.3(a), where lines are drawn to represent the data. Because the first curve in Fig. 4.1(a) showed linear behavior over a considerable time, we assumed that a shorter time would suffice for later anneals

Fig. 4.1. Simple and normalized plots of cesium release vs annealing time at 1250°C for higher-burnup Group A particles (LTI-PyC-coated UO_2 , 22% FIMA).

Fig. 4.2. Simple and normalized plots of cesium release vs annealing time at 1250°C for lower-burnup Group A particles (LTI-PyC-coated UO_2 , 11% FIMA).

Fig. 4.3. Simple and normalized plots of cesium release vs annealing time at 1400°C for Group C particles (LTI-PyC-coated ThO_2 , 3.5% FIMA).

(since the time and cost of extending the anneals were significant). The LTI-PyC-coated Group C particles for which release data are plotted in Fig. 4.3(a), however, were annealed simultaneously with HTI-PyC-coated Group F particles which required a much longer anneal to obtain a constant release; therefore, the Group C anneal at 1400°C was inadvertently carried far enough to show definite depletion. This curve also indicates a possible leveling out at a fractional release of about 5 or 6%. Normalized graphs including the same data are plotted in Figs. 4.1(b), 4.2(b), and 4.3(b) and compared with constant-potential solutions. The normalization is described by Eqs. (3) and (4) in Sect. 2.1.1; the lines in the normalized graphs represent solutions of Eq. (9) in Appendix A. The Group A data fit the linear part of the solution but deviate somewhat in the early breakthrough region in Fig. 4.1(b). The data for sample A-31 show definite evidence of source depletion. The Group C data are seen to fit the constant-potential solution exactly up to where depletion is evident [Fig. 4.3(b)].

4.2.2 Measured and calculated parameters relating to cesium release

Table 4.1 gives values of the apparent diffusion coefficient, D^* , and the driving potential, $C_2(a)$, for cesium diffusion in BISO-coated particles, along with other data related to cesium release. Definitions of the headings are listed under the Guide to Headings at the beginning of Table 4.1. Methods of calculating D^* and $C_2(a)$ with constant-potential diffusion relations and the possible errors involved were discussed in Sect. 2. It should be noted that the initial cesium inventory, M_1^0 , includes all the isotopes of this element. The dimensions of most of the coated particles were measured individually, but many of those for Group A particles, where noted, were taken from averages of measurements on other Group A particles. Data from anneals of bonded fuel pellets are included; the calculations of D^* and $C_2(a)$ from these are believed to be comparable to those from loose particles since the fuel pellets were small and holdup in the matrix was negligible (see Sect. 5.5).

Values of the driving potential or concentration in the outer coating, $C_2(a)$, occasionally deviate from the mean within small groups of the same particles annealed at the same temperature. For example, sample

Table 4.1. Cesium release data from postirradiation anneals of coated particles

Guide to Headings

ℓ	- outer coating thickness = $b - a$, μm
r_k	- kernel, radius, μm
a	- buffer coating radius, μm
b	- outer coating radius, μm
t_o	- breakthrough time - intercept of extrapolated release curve at zero release, hr
m	- slope of experimental FR-vs-t curve, hr^{-1}
M_1^o	- initial fission product inventory - includes all isotopes of subject element, atoms
D^*	- apparent diffusion coefficient, cm^2/sec
$C_2(a)$	- concentration in outer coating at a , atoms/cm^3

Table 4.1. Cesium release data from postirradiation anneals of coated particles

Sample No.	Annealing Temp. (°C)	No. of Particles	ℓ (μm)	r_k (μm)	a (μm)	b (μm)	t_o (hr)	m (hr^{-1})	M_1^o (atoms)	D^* (cm^2/sec)	$C_2(a)$ (atoms/ cm^3)	FR-final (%)	t-final (hr)
Group A: LTI-PyC-Coated UO_2 Particles Irradiated to 11% FIMA													
A-1	1250	10	73.3 ^b	128 ^b	162 ^b	235 ^b	1080	5.31E-6	2.48E15	2.30E-12	2.43E18	0.30	1626
A-2	1250	10	73.3 ^b	128 ^b	162 ^b	235 ^b	493	1.40E-5	2.20E15	5.05E-12	2.59E18	1.65	1626
A-3	1250	a	73.3 ^b	128 ^b	162 ^b	235 ^b	670	1.36E-5	2.31E15 ^b	3.71E-12	3.59E18	0.60	1110
A-4	1250	a	73.3 ^b	128 ^b	162 ^b	235 ^b	1173	1.39E-5	2.31E15 ^b	2.12E-12	6.43E18	0.92	1834
A-5	1400	4	73.3 ^b	128	162 ^b	235	31.8	3.85E-4	2.36E15	7.82E-11	4.93E18	6.13	191
A-6	1400	1	77	124	158	234	17.2	3.04E-3	2.42E15	1.60E-10	2.12E19	18.6	96
A-7	1400	1	73	131	170	242	27.0	9.42E-4	2.71E15	9.14E-11	1.10E19	5.88	89
A-8	1400	1	72	126	158	229	67.0	4.64E-4	2.60E15	3.58E-11	1.48E19	5.55	177
A-9	1400	1	74	121	147	221	24.0	1.13E-3	2.08E15	1.06E-10	1.12E19	16.7	176
A-10	1400	1	82	133	168	250	16.1	2.86E-3	2.69E15	1.93E-10	1.72E19	22.4	96
A-11	1400	1	76.9	127	160	237	23.1	1.39E-3	2.46E15	1.17E-10	1.31E19	10.7	96
A-12	1400	1	81.4	116	146	227	20.0	5.21E-4	1.89E15	1.53E-10	3.49E18	4.05	96
A-13	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	3.79	1.58E-2	1.78E15	6.56E-10	1.82E19	3.49	6
A-14	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	3.40	2.76E-2	2.40E15	7.32E-10	3.84E19	7.18	6
A-15	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	4.20	8.78E-4	1.67E15	5.92E-10	1.05E18	0.16	6
A-16	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	3.57	9.88E-3	2.46E15	6.97E-10	1.48E19	2.40	6
A-17	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	3.04	3.76E-2	1.96E15	8.18E-10	3.82E19	11.13	6
A-18	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	2.23	2.05E-2	2.64E15	1.12E-9	2.05E19	7.74	6
A-19	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	3.12	2.27E-2	2.29E15	7.97E-10	2.77E19	6.55	6
A-20	1500	1	73.3 ^b	128 ^b	162 ^b	235 ^b	3.06	2.25E-2	2.65E15	8.13E-10	3.11E19	6.61	6

Table 4.1 (continued)

Sample No.	Annealing Temp. (°C)	No. of Particles	ℓ (μm)	r_k (μm)	a (μm)	b (μm)	t_o (hr)	m (hr^{-1})	M_1^o (atoms)	D^* (cm^2/sec)	$C_2^{(a)}$ (atoms/ cm^3)	FR-final (%)	t-final (hr)
A-21	1600	1	71.4	127	164	235	0.90	5.42E-2	2.22E15	2.63E-9	1.88E19	16.8	4
A-22	1600	1	65.2	124	156	221	0.95	8.73E-2	2.21E15	2.07E-9	3.89E19	20.8	4
A-23	1600	1	70.3	127	164	235	1.1	5.25E-2	2.36E15	2.08E-9	2.40E19	14.7	4
A-24	1600	1	63.8	127	164	228	1.27	7.80E-2	2.30E15	1.48E-9	4.57E19	19.7	4
A-25	1600	1	65.4	118	148	213	0.76	7.68E-2	1.87E15	2.61E-9	2.52E19	22.1	4
A-26	1600	1	61.0	129	173	234	0.87	4.44E-2	2.42E15	1.99E-9	1.79E19	13.9	4
A-27	1600	1	69.0	132	162	231	0.82	9.07E-2	2.54E15	2.67E-9	3.51E19	22.5	4
A-28	1600	4	73.3 ^b	128	162 ^b	235 ^b	1.97	1.65E-2	2.58E15	1.26E-9	1.43E19	5.15	5
Group A: LTI-PyC-Coated UO_2 Particles Irradiated to 22% FIMA													
A-29	1250	a	73.3 ^b	128 ^b	162 ^b	235 ^b	350	1.22E-4	3.42E15 ^b	7.11E-12	2.50E19	30.0	2800
A-30	1250	a	73.3 ^b	128 ^b	162 ^b	235 ^b	195	1.36E-4	3.42E15 ^b	1.28E-11	1.54E19	10.7	1020
A-31	1250	8	73.3 ^b	128 ^b	162 ^b	235 ^b	250	2.24E-4	3.92E15	9.95E-12	3.74E19	20.3	1626
A-32	1400	1	73.3 ^b	128 ^b	162 ^b	235 ^b	20.3	1.03E-3	3.52E15	1.23E-10	1.25E19	9.09	191
A-33	1400	1	73.3 ^b	128 ^b	162 ^b	235 ^b	33.3	2.38E-4	3.76E15	7.47E-11	5.08E18	3.75	191
A-34	1400	1	73.3 ^b	128 ^b	162 ^b	235 ^b	20.8	4.42E-4	3.96E15	1.20E-10	6.20E18	5.65	191
A-35	1400	1	73.3 ^b	128 ^b	162 ^b	235 ^b	33.6	9.10E-4	2.83E15	7.40E-11	1.48E19	14.25	191
A-36	1600	4	73.3 ^b	128 ^b	162 ^b	235 ^b	1.37	2.31E-2	3.97E15	1.82E-9	2.15E19	8.44	5
Group B: LTI-PyC-Coated UO_2 Particles Irradiated to 13% FIMA													
B-1	1600	1	72.6	60.6	90.9	164	8.8	8.11E-3	2.31E14	3.77E-10	7.30E18	7.46	18
B-2	1600	1	67.1	55.3	98.5	166	9.2	7.99E-3	1.72E14	2.27E-10	5.51E18	7.03	18

Table 4.1 (continued)

Sample No.	Annealing Temp. (°C)	No. of Particles	ℓ (μm)	r_k (μm)	a (μm)	b (μm)	t_o (hr)	m (hr^{-1})	M_1^o (atoms)	D^* (cm^2/sec)	$C_2^{(a)}$ (atoms/ cm^3)	FR-final (%)	t-final (hr)
Group C: LTI-PyC-Coated ThO_2 Particles Irradiated to 3.5% FIMA													
C-1	1400	1	87.8	151	177	265	155	1.38E-5	7.29E14	2.30E-11	1.81E17	42.97	3630
C-2	1400	1	99.0	143	163	262	235	1.41E-5	7.36E14	1.93E-11	2.77E17	3.04	3755
C-3	1400	1	96.2	146	171	267	170	1.63E-5	7.20E14	2.52E-11	2.16E17	3.96	3755
C-4	1400	1	97.9	145	168	266	133	1.60E-5	7.20E14	3.34E-11	1.66E17	4.42	3755
C-5	1600	1	86.7	140	162	248	16.2	4.15E-4	6.05E14	2.15E-10	5.56E17	82.3	781
C-6	1600	1	72	146	174	246	11.6	2.55E-4	6.62E14	2.07E-10	3.05E17	71.8	781
Group D: LTI-PyC-Coated UC_2 Particles Irradiated to 13% FIMA													
D-1	1400	1	65.1	60.0	113	178	74	6.59E-5	3.85E14	2.65E-11	6.89E17	1.56	302
D-2	1400	1	67.3	61.4	104	171	101	1.99E-4	2.94E14	2.08E-11	2.37E18	4.07	302
D-3	1400	1	57.2	64.1	124	181	102	9.14E-5	3.82E14	1.48E-11	1.33E18	1.83	302
D-4	1600	1	62.6	51.5	108	171	5.3	3.50E-3	2.09E14	3.42E-10	1.61E18	4.44	18
D-5	1600	1	74.5	58.6	94	169	6.5	3.24E-3	2.61E14	3.95E-10	2.22E18	3.73	18
Group E: HTI-PyC-Coated UC_2 Particles Irradiated to 13% FIMA													
E-1	1400	1	40.4	54.6	102	143	62	1.40E-4	2.30E14	1.22E-11	1.62E18	3.48	302
E-2	1400	1	42.5	52.0	102	144	92	1.86E-4	1.79E14	9.09E-12	2.34E18	4.05	302
E-3	1400	1	48.5	55.2	122	171	87	1.22E-4	2.26E14	1.25E-11	1.13E18	2.66	302
E-4	1600	1	47.2	50.5	100	148	7.2	1.36E-2	1.79E14	1.42E-10	1.21E19	14.6	18
E-5	1600	1	42.6	53.0	108	150	7.0	1.30E-2	2.03E14	1.20E-10	1.28E19	14.4	18

Table 4.1 (continued)

Sample No.	Annealing Temp. (°C)	No. of Particles	ℓ (μm)	r_k (μm)	a (μm)	b (μm)	t_o (hr)	m (hr^{-1})	M_1^o (atoms)	D^* (cm^2/sec)	$C_2^{(a)}$ (atoms/ cm^3)	FR-final (%)	t-final (hr)
Group F: HTI-PyC-Coated ThO_2 Particles Irradiated to 3.5% FIMA													
F-1	1400	1	85.2	138	155	240	1500	3.20E-7	6.94E14	2.24E-12	5.00E16	0.0707	3755
F-2	1400	1	85.0	138	155	240	1490	1.02E-7	6.67E14	2.24E-12	1.53E16	0.0308	3755
F-3	1400	1	86.2	139	155	241	1500	2.66E-7	7.01E14	2.29E-12	4.15E16	0.0629	3755
F-4	1400	1	83.7	138	164	247	1460	5.98E-7	7.13E14	2.22E-12	8.78E16	0.138	3755
F-5	1600	1	85.0	138	157	242	240	3.31E-5	4.64E14	1.39E-11	5.45E17	1.86	781
F-6	1600	1	87.2	157	175	263	273	2.15E-5	1.03E15	1.29E-11	7.20E17	1.16	781
Group G: HTI-PyC-Coated ThO_2 Particles Irradiated to 3.5% FIMA													
G-1	1600	1	165	235	307	471	~4E2	~2E-6	4.01E15	~3E-11	~2E16	0.018	781
G-2	1600	1	244	238	318	482	~4E2	~4E-8	3.96E15	~7E-11	~2E16	0.015	781
Group H: LTIA-PyC-Coated ThO_2 Particles Irradiated to 3.5% FIMA													
H-1	1600	1	174	248	310	483	125	3.07E-4	4.23E15	1.12E-10	2.98E18	17.7	781
H-2	1600	1	188	234	310	497	132	3.12E-4	3.65E15	1.24E-10	2.48E18	14.7	781

^aFuel pellet containing ~ 80 LTI-PyC-coated UO_2 particles.

^bAverage postirradiation dimensions from 35 coated particles.

A-15 has a $C_2(a)$ value which is a factor of 10 less than the other coated particles annealed at 1500°C in the same multitube crucible. The slope, m , for this sample is correspondingly low. No explanation is currently apparent for these differences.

Samples A-5, A-12, A-33, and A-34 also have low slopes and concentrations. Samples A-5 and A-32 through A-35 were annealed in the same multitube crucible. The curves for this series are lacking in detail because the crucible containing these samples was being alternated with a long-term anneal, and a mixup caused the final annealing step to last 1 week instead of 6 hr as planned. Although the intercepts could be placed with some confidence, the slopes could only be estimated. The data were included since they furnish the only information on the cesium diffusion coefficient at 1400°C for the Group A coated particles irradiated to 22% FIMA.

4.3 Experimental Results on the Release of Barium, Strontium, and Cerium

Results on the release of barium, strontium, and cerium during post-irradiation anneals were obtained either in scoping experiments or as by-products of the cesium release experiments. The data were plotted as a fractional release vs the square root of annealing time, which seemed to produce the most linear representation. The breakthrough times, t_0 , were obtained from the intercepts of the linear portions of the curves, from which the approximate apparent diffusion coefficients, D^* , were calculated using the relation $D^* = l^2/6t_0$. It is recognized that this is only an approximate relation where depletion and source region control are dominant, as discussed in Sect. 2.4.2.

4.3.1 Graphs of fission product release vs annealing time

The graphical results from five separate annealing experiments will be described below in order of increasing temperature.

Four Group D and four Group E coated particles from the C1-28 irradiation experiment were annealed simultaneously in the multitube crucible at 1150°C. The FR-vs- $\sqrt{t}$ plots for barium and cerium are shown in Figs. 4.4 - 4.7. Cesium was not released. The cerium data in Figs. 4.4 and 4.5 showed wide scatter, and the possible variation in the intercepts taken from these curves is about a factor of 2: The total cerium

Fig. 4.4. Cerium release vs square root of time at 1150°C for Group D particles (LTI-PyC-coated UC₂, 13% FIMA).

Fig. 4.5. Cerium release vs square root of time at 1150°C for Group E particles (HTI-PyC-coated UC₂, 13% FIMA).

Fig. 4.6. Barium release vs square root of time at 1150°C for Group D particles (LTI-PyC-coated UC₂, 13% FIMA).

Fig. 4.7. Barium release vs square root of time at 1150°C for Group E particles (HTI-PyC-coated UC₂, 13% FIMA).

release from the LTI-coated Group D particles averaged about 13% at 71 hr, while that from the HTI-coated Group E particles was less than 2%. The barium release data in Figs. 4.6 and 4.7 are more consistent. A trapped fraction averaging about 73% of the total produced is indicated by the Group D data. The Group E data do not indicate any limitation at an average release of 20% after 39 hr of annealing.

Two other sets consisting of four coated particles each from Groups D and E, respectively, were annealed at 1400°C. The release results for cesium were reported in Sect. 4.2; the barium had already decayed when these data were obtained. The release of cerium vs $\sqrt{t}$ is plotted in Fig. 4.8. The intercepts of these curves can only be estimated; however, they must lie between 0 and 9 hr, which yields a value for D of greater than 1×10^{-10} cm²/sec. The significant result from these experiments is the magnitude of the release. Seventy-five percent of the total cerium was released from Group D, LTI-coated particles and 89% from Group E, HTI-coated particles in about 35 hr. Both curves nearly leveled off below 100% release, indicating a trapped fraction with a much slower diffusion process.

During cesium release studies of Groups C and F coated particles at 1400°C, the bremsstrahlung activity was determined vs time. Since all short-lived isotopes had decayed and cesium had not yet penetrated the coatings during the early part of the anneal, it was assumed that the bremsstrahlung activity was representative of the strontium beta activity. The coated particles were removed after each annealing step, and the tungsten tubes from the multitube crucible were placed in the same geometry over a sodium iodide detector to determine the count rate. The results of bremsstrahlung activity vs $\sqrt{t}$ are plotted in Fig. 4.9.

The release of barium and strontium was measured in some early annealing experiments using trace-irradiated LTI-PyC-coated UO₂ particles from Group A. These particles had been irradiated for 6 hr in a neutron flux of about 10^{13} neutrons/cm² at a temperature of < 800°C. Insufficient cesium was produced for analysis, and the anneals had to be completed before the decay of the 9.7-hr ⁹¹Sr, generally within 43 hr after irradiation. Graphs of the ¹⁴⁰Ba and ⁹¹Sr release fractions at 1500°C are shown in Figs. 4.10 and 4.11. All of the barium

Fig. 4.8. Cerium release vs square root of time at 1400°C for Group D (LTI-PyC-coated UC₂, 13% FIMA) and Group E (HTI-PyC-coated UC₂, 13% FIMA) particles.

Fig. 4.9. Bremsstrahlung from released strontium vs square root of time at 1400°C for Group C (LTI-PyC-coated ThO₂, 3.5% FIMA) and Group F (HTI-PyC-coated ThO₂, 3.5% FIMA) particles.

Fig. 4.10. Barium release vs square root of time at 1500°C for trace-irradiated Group A particles (LTI-PyC-coated UO_2).

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Fig. 4.11. Strontium release vs square root of time at 1500°C for trace-irradiated Group A particles (LTI-PyC-coated UO_2).

and strontium release curves at 1500°C except for A-41 exhibit an increase in slope occurring some time after the initial breakthrough. This variation in behavior is similar to that of the cesium release-vs-time curves for Group C particles where an abrupt increase in cesium source potential was noted (see Sect. 5.4). Intercepts were taken from the initial part of the curves for the calculation of diffusion coefficients. Trapped fractions are indicated in the shapes of the A-38 barium release curve and in the A-37, A-38, and A-39 strontium release curves.

The barium and strontium release fractions from anneals at 1700°C of Group A coated particles are plotted vs $\sqrt{t}$ in Figs. 4.12 and 4.13. The curve showing barium release from sample A-45 exhibits a steep slope and levels off at about 53%. The A-43 and A-44 barium release curves almost coincide with each other on a more moderate slope. The slopes and intercepts of the strontium release curves of the A-43, A-44, and A-45 coated particles agree closely. The fractional release of strontium from the A-44 and A-45 samples almost levels out with time at about 36% and 15% respectively.

4.3.2 Coated-particle dimensions and other data

The annealing temperature, coated-particle dimensions, total fission product inventory, cumulative fractional release at the end of annealing time, and the final annealing time are given in Table 4.2. Since the role of the kernel and buffer are far more uncertain in the release of barium, strontium, and cerium than for cesium, the data are scattered, and the graphs are difficult to interpret, the diffusion coefficients from individual coated particles are not presented here. Approximate averages are given in the discussion in Sect. 5.6.

5. DISCUSSION OF RESULTS

The fission product release data presented in Sect. 4 has provided a range of cesium diffusion coefficients in different types of pyro-carbon coatings as a function of temperature. A constant-potential cesium release and a possible concentration limit in the coatings are

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Fig. 4.12. Barium release vs square root of time at 1700°C for trace-irradiated Group A particles (LTI-PyC-coated UO_2).

Fig. 4.13. Strontium release vs square root of time at 1700°C for trace-irradiated Group A particles (LTI-PyC-coated UO_2).

Table 4.2. Barium, cerium, and strontium release data from postirradiation anneals of coated particles

Guide to headings:

- ℓ - outer coating thickness = $b - a$
 r_k - kernel radius
 a - buffer coating radius
 b - outer coating radius
 M_1^0 - initial fission product inventory - includes all isotopes of subject element

Sample No.	Fission product	Annealing temp. (°C)	No. of particles	ℓ (μm)	r_k (μm)	a (μm)	b (μm)	M_1^0 (atoms)	FR-final (%)	t-final (hr)
Group A: LTI-PyC-coated UO ₂ particles - neutron activated										
A-37	Sr	1500	1	73 ^a	128 ^a	162 ^a	235 ^a	2.7E12	29	180
	Ba							3.0E12	24	180
A-38	Sr	1500	1	73 ^a	128 ^a	162 ^a	235 ^a	1.9E12	23	180
	Ba							2.1E12	53	180
A-39	Sr	1500	1	73 ^a	128 ^a	162 ^a	235 ^a	1.9E12	16	180
	Ba							2.1E12	31	180
A-40	Sr	1500	1	73 ^a	128 ^a	162 ^a	235 ^a	2.7E12	12	66
	Ba							3.0E12	18	66
A-41	Sr	1500	1	73 ^a	128 ^a	162 ^a	235 ^a	2.5E12	3	180
	Ba							2.7E12	2	180
A-42	Sr	1700	1	73 ^a	128 ^a	162 ^a	235 ^a	8 E13	84	9
	Ba							8 E13	88	9
A-43	Sr	1700	1	73 ^a	128 ^a	162 ^a	235 ^a	8 E13	66	3
	Ba							8 E13	67	3
A-44	Sr	1700	1	73 ^a	128 ^a	162 ^a	235 ^a	3 E12	39	3
	Ba							3 E12	65	3
A-45	Sr	1700	2	73 ^a	128 ^a	162 ^a	235 ^a	7 E12	15	1
	Ba							8 E12	53	1

Table 4.2 (continued)

Sample No.	Fission product	Annealing temp. (°C)	No. of particles	ℓ (μm)	r_k (μm)	a (μm)	b (μm)	M_1^0 (atoms)	FR-final (%)	t-final (hr)
Group D: LTI-PyC-coated UC ₂ particles irradiated to 13% FIMA										
D-6	Ce	1150	1	58 ^a	57 ^a	110 ^a	168 ^a	2 E14	10	71
	Ba							8 E13	26	55
D-7	Ce	1150	1	58 ^a	57 ^a	110 ^a	168 ^a	2 E14	17	71
	Ba							8 E13	20	39
D-8	Ce	1150	1	58 ^a	57 ^a	110 ^a	168 ^a	3 E14	12	71
	Ba							1 E14	24	39
D-9	Ce	1150	1	58 ^a	57 ^a	110 ^a	168 ^a	2 E14	14	71
	Ba							1 E14	39	39
D-1	Ce	1400	1	65	60	113	178	2 E14	81	80
D-2	Ce	1400	1	67	61	104	171	3 E14	81	80
D-3	Ce	1400	1	57	64	124	181	3 E14	65	80
D-10	Ce	1400	1	62	56	119	181	2 E14	88	80
Group E: HTI-PyC-coated UC ₂ particles irradiated to 13% FIMA										
E-6	Ce	1150	1	43	66	105	148	3 E14	0.5	71
	Ba							1 E14	21	55
E-7	Ce	1150	1	46	65	104	150	2 E14	2	55
	Ba							1 E14	22	39
E-8	Ce	1150	1	42	57	100	142	2 E14	0.8	55
	Ba							9 E13	16	39
E-9	Ce	1150	1	40	59	119	159	2 E14	2	71
	Ba							8 E13	22	39
E-1	Ce	1400	1	40	55	102	143	2 E14	92	80
E-2	Ce	1400	1	42	52	102	144	2 E14	97	80
E-3	Ce	1400	1	48	55	122	171	2 E14	94	80
E-10	Ce	1400	1	43	58	117	160	2 E14	89	80

^a Average dimensions.

indicated by the data for anneals of coated particles with the higher burnups (10 to 22% FIMA). Trapping of some of the cesium within the kernel is indicated in the anneals that were carried to complete depletion, and an unexplained rise in cesium potential is noted in the anneals of a few low-burnup particles. Distribution of fission products in the components of an annealed fuel pellet, including the kernels and coatings of the fuel particles, was determined by disintegration and analysis of the fuel pellet. Release-vs- $\sqrt{t}$ curves of barium, strontium, and cerium were difficult to interpret; however, approximate diffusion coefficients were determined.

5.1 The Apparent Cesium Diffusion Coefficients

The logarithms of the apparent diffusion coefficients for cesium in the pyrocarbon coatings of the various coated particle groups are plotted vs reciprocal temperature in Fig. 5.1. The lines are linear least-squares fits of the data presented, and the activation energies tabulated on the figure were calculated from the slopes. A possible effect of concentration is indicated by the difference between the lines calculated for the data at two burnups of Group A coated particles.

No systematic correlation of diffusion coefficients with the measured coating parameters other than thickness was obtained. However, if we classify the coatings according to types as discussed earlier, we find that the average of the diffusion coefficients of the LTI groups at 1400°C is approximately ten times that of the HTI groups. The difference in the structure of the HTI PyC and the LTI PyC is discussed in Sect. 3.1. The data are replotted according to coating types in Fig. 5.2; 95% confidence limits are given. It should be noted, however, that confidence limits are usually based on random experimental errors while those given here are based on variations due to differences between the properties of various batches of coatings. The confidence limits would be much narrower for the cesium release from any given batch of coated particles. Burnette⁴⁸ averaged GAC and ORNL results to obtain diffusion coefficients for cesium in LTI PyC according to the equation

$$D \text{ (cm}^2\text{/sec)} = 0.42 \exp (-3.9 \times 10^4/T),$$

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Fig. 5.1. Diffusion coefficients for cesium in pyrocarbon vs reciprocal temperature: individual data.

Fig. 5.2. Diffusion coefficients for cesium in pyrocarbon vs reciprocal temperature: averaged data.

and Gethard and Zumwalt⁴⁹ obtained the relation

$$D \text{ (cm}^2\text{/sec)} = 9.7 \times 10^{-7} \exp (-2.11 \times 10^4/T)$$

for cesium in HTI PyC.

5.2 Evidence of a Concentration Limit in the Outer Coating

Averages of cesium concentrations in the outer coatings at the buffer-to-outer-coating interface, $C_2(a)$, taken from Table 4.1, are presented in Table 5.1. It should be noted that these are calculated from the constant-potential equations and, in those cases where kernel depletion occurs, represent an average concentration that is less than the initial driving potential. Comparison of the concentrations, $C_2(a)$, calculated from release data of Group A coated particles irradiated to 11% and 22% FIMA, show approximately equal average concentrations except for the lower temperature anneals of the coated particles irradiated to 11%. This is offered as evidence that a cesium concentration limit has been reached, although it is not clear whether this limit is associated with the solubility of cesium in pyrocarbon, a property of the kernel, or the vapor pressure of cesium over liquid cesium that may be present in the buffer. In the latter case, however, the vapor pressure and hence the source potential and the concentration, $C_2(a)$, would be expected to increase with temperature. The concept of a limiting concentration is discussed in ref. 1. The lower concentrations in the coatings of Group A coated particles irradiated to 11% FIMA and annealed at the lower temperatures can be explained as an effect of a larger trapped fraction at the lower temperatures. An increase in the concentration, $C_2(a)$, with annealing temperature was not observed for the Group A-22% FIMA particles, which would be expected to contain larger amounts of cesium.

5.3 Evidence of a Trapped Fraction of Cesium

"Trapped fraction," as used here, is defined as the fraction of total fission products produced that is trapped at the annealing temperature. The trapping is considered permanent, at least to the extent that the release of fission product from the traps over a period of several hundred hours will be insignificant. It is recognized that a very slow diffusion process may be involved.

Table 5.1. Averages of cesium concentrations, $C_2(a)$

Group	Burnup (% FIMA)	Annealing temp. (°C)	Av $C_2(a)$ (atoms/cm ³)
A	11	1250	3.8E18
A	11	1400	1.2E19
A	11	1500	2.7E19
A	11	1600	2.7E19
A	22	1250	2.6E19
A	22	1400	~ 9.6E18
A	22	1600	2.2E19
B	13	1600	6.4E18
C	3.5	1400	2.1E17
C	3.5	1600	4.3E17
D	13	1400	1.5E18
D	13	1600	1.9E18
E	13	1400	1.7E18
E	13	1600	1.2E18
F	3.5	1400	4.9E16
F	3.5	1600	6.3E17
G	3.5	1600	~ 2E16
H	3.5	1600	2.7E18

The graph of cesium release vs time from an anneal of sample C-6 at 1600°C (Fig. 5.3) approaches a limiting release of 73%, indicating a trapped fraction of about 23% of the total cesium produced in the coated particle. Only three anneals, C-2, C-5, and C-6, were carried to the point where the release rate leveled out to zero. The trapped fraction can be definitely established for these coated particles. Several other curves showed evidence of depletion from which a trapped-fraction asymptote could be estimated. The ranges of trapped fractions, together with the burnup, the kernel material, and the annealing temperature, are tabulated below:

Burnup (% FIMA)	Original kernel material	Trapped fraction of cesium (%)		
		At 1250°C	At 1400°C	At 1600°C
3.5	ThO ₂	ND ^a	65-95	18-28
11	UO ₂	ND ^a	65-75	60-70
22	UO ₂	70	ND ^a	ND ^a

^aND - not determined.

These data suggest that the trapped fraction may decrease with increasing temperature. Further research is necessary to prove and quantify this relation and to establish any effects of kernel composition and burnup. Future experiments to obtain complete depletion could be shortened by separating the coated particle components and annealing these separately; of course, care must be taken to maintain the environment so that reactions do not occur.

5.4 Abrupt Changes in Source Potential

The release of cesium vs time from sample C-1 is plotted in Fig. 5.4(a). This curve is similar to a normal constant-potential curve except for the extended transient region below 10% release; also, the release-vs-time graphs of the C-2, C-3, and C-4 samples duplicated the path of the C-1 curve almost exactly up to 1100 hr and continued on a linear line to 1400 hr, at which time depletion effects were indicated [Fig. 4.3(a)]. The LTI-PyC-coated ThO₂ particles comprising the C-1, C-2, C-3, and C-4

Fig. 5.3. Cesium release vs annealing time at 1600°C for Group C particles (LTI-PyC-coated ThO_2 , 3.5% FIMA).

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Fig. 5.4. Cesium release-vs-time plots, showing rise in source potential for Group C particles (LTI-PyC-coated ThO₂, 3.5% FIMA).

samples were obtained from the same batch, irradiated in the same capsule, and annealed at the same time in the multitube crucible. The normalized plot of the C-1 data in Fig. 5.4(b) shows the excellent fit of the early part of the data up to 1100 hr with the solution to the constant-potential equation (if the data beyond 1100 hr are ignored). The breakthrough time, t_0 , and the slope, m , were taken from the early part of the curve. Figure 5.4(c) is also a normalized plot of the same data, including that beyond 1100 hr, but t_0 and m in this case were taken from the intercept of the extrapolation from the later part of the curve. The solutions to the constant-potential equation are represented by the solid lines in Figs. 5.4(b) and (c).

This anomalous behavior indicates an increase in source potential, which is probably due to some change in kernel structure. The same behavior was noted in the release-vs-time curves of samples C-5 and C-6 (Fig. 5.3) for anneals at 1600°C but was not evident in the anneals of Group F HTI-PyC-coated ThO_2 particles, which were also irradiated in the same capsule and annealed simultaneously with the Group C particles in the multitube crucible. Coating failure was ruled out as the cause of abrupt rise in release rate since no ^{85}Kr was detected during the anneals. Curves of similar shape were obtained in the release of barium and strontium from LTI-PyC-coated UO_2 that had been trace irradiated (Figs. 4.10 and 4.11), but the interpretation may not be the same in the two cases because of significant differences in absorptivity, chemical potentials, and volatility.

The only explanation advanced so far is that thermal cycling during the anneals caused the kernel to crack and spall.

5.5 Distribution of Fission Products in an Annealed Fuel Pellet

The A-29 fuel pellet, which contained approximately 80 LTI-PyC-coated UO_2 particles, was annealed for 2500 hr at 1250°C. A drawing of the fuel pellet, the graphite can, and the furnace tube is shown in Fig. 2.5. The cesium release data are reported in Table 4.1; a graph of the release vs time is shown in Fig. 4.1(a).

After the annealing had been completed, the fuel pellet was disintegrated and the coated particles and matrix were separated. Twenty

of the coated particles, the matrix, and the graphite can were analyzed for ^{137}Cs and ^{144}Ce . Six coated particles were cracked, and the coatings and kernels were separated and analyzed for ^{90}Sr , ^{137}Cs , and ^{144}Ce . The distribution of the fission products in the various components is given in Table 5.2. The total activities for ^{137}Cs and ^{144}Ce were obtained from gamma-ray analyses. The total ^{90}Sr was calculated from analyses of ^{144}Ce and irradiation data.

The distribution shows that a large fraction of cesium is held in the coating (consisting of porous buffer and high-density outer coating), while only small amounts of strontium and cerium are retained in this component. In the porous matrix and graphite can, on the other hand, very little cesium was held up while 3% of the strontium was absorbed.

5.6 Barium, Strontium, and Cerium Results

The data for barium, strontium, and cerium are more difficult to interpret than those for cesium because barium, strontium, and cerium are less volatile, absorbed more strongly in porous carbon, and diffuse through dense pyrocarbon more rapidly than does cesium. Hence their retention in the kernel and buffer regions would be expected to influence the shapes, slopes, and intercepts of the release-vs-time curves more than in the case of cesium. Norman et al.⁵⁰ have calculated fractional release-vs- $\sqrt{t}$ solutions for coated particles with dimensions similar to those used in these experiments by means of the Slider computer program. They found that in instances where the kernel and coating diffusion coefficients were nearly the same, variations in the slopes of the release curves could be caused by changing either the kernel diffusion coefficient or the partition coefficient. Increases in the kernel diffusion coefficient increased the slope without changing the intercept. Changing the coating diffusion coefficient displaced the curve on the $\sqrt{t}$ axis without changing the slope. Therefore, it may not be possible to determine more than approximate diffusion coefficients from these data.

The diffusion coefficients for strontium, barium, and cerium calculated from the average intercepts are given in Table 5.3. Also included are results obtained for strontium in a composite coating (Lot 1031C)

Table 5.2. Distribution of fission products in bonded fuel pellet A-29
after a 2500-hr anneal at 1250°C

Component	Fraction of total fission products (%)		
	Cesium	Strontium	Cerium
Core	41	68	97
Coating	34	0.5	3
Matrix	0.08	3	0
Released from bonded bed	25	28	0
Graphite can	0.007	ND ^a	0

^aND = not determined.

Table 5.3. Diffusion coefficients for barium, cerium, and strontium in pyrocarbon

Temp. (°C)	Group or experiment	Diffusion coefficient ^c			Type of Coating
		Sr	Ba	Ce	
1150	G & Z ^a	1.86E-9	-	-	HTI
	D	-	1.0E-9	~3.2E-10	LTI
	E	-	1.1E-10	~2.7E-11	HTI
	R ^b	9E-9	6E-10	-	Composite coating
1400	C	~7.7E-9	-	-	LTI
	F	~3.6E-9	-	-	HTI
	G & Z ^a	2.35E-8	-	-	HTI
1500	A	2E-8 to ~5.6E-9	~4.1E-9	-	LTI
	G & Z ^a	5.31E-8	-	-	HTI
1700	A	4.7E-7	4.3E-8	-	LTI
	G & Z ^a	2.11E-7	-	-	HTI

^aGethard and Zumwalt, ref. 49.

^bRosenberg et al., ref. 51.

^cDiffusion coefficients obtained for Groups A, C, D, E, and F should be considered approximate values (see text).

by Rosenberg et al.⁵¹ and the diffusion coefficients for strontium in HTI-PyC obtained by Gethard and Zumwalt⁴⁹ according to the relation

$$D = 4.4 \times 10^{-2} \exp \left(-\frac{48,000}{RT} \right) \text{ cm}^2/\text{sec} ,$$

where R is the gas constant, in cal/g·mole, and T is the absolute temperature, in °K.

6. RECOMMENDATIONS

In order to calculate the release of cesium from intact coated particles during irradiation, we need to know the apparent diffusion coefficient, D^* , the driving potential, $C_2(a)$, the partition coefficient, ϕ [ratio of source potential to $C_2(a)$], and the extent of trapping in the kernel. We assume rapid migration of cesium in the kernel and buffer regions. For other fission products, the rate of diffusion in these regions remains to be determined. We will also assume that the neutron flux and the burnup will not change D^* , ϕ , and the limit of $C_2(a)$ significantly, although the effect of fast neutron fluences needs to be examined. Effects of neutron flux and burnup on the extent of trapping in the kernel would be expected.

6.1 The Diffusion Coefficient

The diffusion coefficients for cesium in fuel particle coatings have been determined for a large number of samples with different properties. Because of the presence of too many variables and a lack of sufficient characterization of the coatings, it is still impossible to predict precise values of D^* from a knowledge of measurable coating characteristics. If further work in this area were attempted, a means of determining complete characteristics of irradiated coatings, including the amorphous/crystalline carbon ratio and a definition of the microstructural detail, should be provided. In lieu of the determination of precise values of D^* from coating characteristics, we have available a range of D^* values from which limiting rates of release may be obtained. For a more accurate value, the diffusion coefficient needs to be determined for reference fuel particles. One also needs to verify

that diffusion coefficients obtained in postirradiation experiments are applicable to calculations of fission product release during irradiation under realistic conditions for HTGRs. We plan to analyze HTGR fuel particles irradiated over a wide range of temperature and burnup conditions to provide at least a rough comparison of fission product release during irradiation with that calculated using diffusion coefficients obtained from postirradiation annealing experiments.

6.2 Limit of Cesium Concentration in the Coating

The evidence that the constant potential observed in some experiments is due to a limit of cesium solubility in the outer coating rather than a constant vapor pressure over excess cesium liquid is not definite; sufficient results are needed to prove that the observed trends do not result from scatter in the data. Additional postirradiation anneals of Group A coated particles irradiated to 20% are planned in an effort to improve the data.

6.3 The Partition Coefficient

To date, partition coefficients have not been measured. The partition coefficient may be determined from cesium release curves of coated particles annealed to complete depletion.

6.4 Trapped Fraction of Cesium

We cannot assume that numerical results obtained in postirradiation experiments will be applicable to determine fission product retention during irradiation since the fission fragments would be continuously disrupting the kernel structure in a neutron flux. Under this condition, it is difficult to understand how fission products could remain trapped. On the other hand, an indication that the trapped fraction may be significant even during irradiation is given in the results of irradiation experiments at low burnups on bare UO_2 and UC_2 particles by Reagan, Morgan, and Sisman.⁵² These particles retained 79% and 56% of the total cesium (analyzed) during irradiation at 1200°C to burnups of 5% and 3.5% respectively; a large fraction of strontium and barium escaped. About one-third of the cerium was released from the UC_2 particles, while very

little left the UO_2 particles. More than 95% of the zirconium and ruthenium were retained. In another experiment in which irradiation was carried out at 1250°C to a burnup of 6% FIMA,⁵² BISO-coated UO_2 particles lost nearly half of the strontium and barium. Although 97% of the analyzed cesium was retained, the total analyzed amounted to only 32% of that calculated.

Evidence from the postirradiation annealing experiments indicates that, if the fuel is removed from the reactor or if the fission rate is reduced to zero, some quantity of fission products will reside in permanent traps at any given temperature; the rest is free to migrate to the surface by a diffusion-like process. It may be impossible to analyze the separate processes involved in fission product migration in the fuel during irradiation. However, for the purpose of determining fission product release (if we assume that permanent trapping is not available), only the overall behavior needs to be known, that is, the rate of release of the fission products from the kernels as a function of burnup, temperature, neutron flux, and kernel characteristics. This will be tested by comparing release data from irradiation experiments with worst-case calculations.

In order to prove that permanent trapping in the fuel may occur during irradiation, it may be of value to anneal irradiated fuel particles to complete depletion of available fission products and then to re-irradiate the fuel particles for a short period. The particles would subsequently be annealed again to determine to what extent the fission fragments had stirred the trapped fission products. Fission product inventories and distributions between the coated particles and capsule or furnace components would be needed for both irradiation and annealing experiments. If the release of fission products after the first post-irradiation anneal was significantly low during reirradiation and the second anneal, trapping during irradiation would be indicated. Further experiments could be performed for more complete evaluation.

6.5 Effect of Fast Neutrons on Diffusion Parameters

In order to determine the effect of fast-neutron exposure on the coating diffusion parameters, one needs to obtain identical coated

particles irradiated to the same burnups, but to different levels of fast-neutron exposure. This would require separate irradiations in two different reactors. If the difference in neutron flux levels is too great to allow irradiation of the same fuel kernel in both irradiations, the thorium or thorium-uranium and uranium kernels of the same diameter could be coated simultaneously in the same coater and could later be separated by activation analysis for the irradiation and annealing experiments.

7. CONCLUSIONS

These studies have shown that pyrocarbon coatings retain krypton, xenon, iodine, and tellurium but are permeable to cesium, strontium, barium, and cerium. The last three elements diffuse through dense pyrocarbon 30 to more than 100 times faster than cesium, and are retained to a greater extent by the kernels of coated particles than by the coatings. Although limited results were obtained and presented for other fission products, extensive experiments on cesium release provided ranges of the apparent diffusion coefficients for cesium in various types of pyrocarbon as a function of temperature, from which estimates of maximum rates of release during irradiation can be calculated. It was shown that the diffusion coefficient is affected more strongly by the type of pyrocarbon (i.e., HTI or LTI) than by slight variation in density or anisotropy and that this difference may be more than a factor of 10, the LTI pyrocarbon having the higher diffusion coefficient at a temperature of 1400°C or above.

It was also shown that a certain amount of cesium remains trapped in the coated particle during postirradiation anneals. It is expected that this fraction will change as a function of temperature, concentration or burnup, neutron flux, and kernel material. A concentration limit of approximately 2×10^{19} atoms/cm³ was indicated for cesium in the high-density pyrocarbon outer coating.

Additional postirradiation experiments are planned to determine the cesium partition coefficients and the trapped fraction of cesium as functions of temperature, burnup, and material, and to verify the existence of a concentration limit in the coatings.

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9. NOMENCLATURE

a	Position of source zone-coating interface, cm
b	Outer boundary of coated particle, cm
BISO	Duplex pyrocarbon coating featuring porous buffer inner layer with dense isotropic outer layer
$C_1(t)$	Total fission product concentration in source zone, atoms/cm ³
$C_1^*(t)$	Mobile fission product concentration in source zone, atoms/cm ³
$C_2(a)$	Fission product concentration in outer coating at source zone-coating interface with constant potential, atoms/cm ³
$C_2(a,t)$	Fission product concentration in outer coating at source zone-coating interface with changing potential, atoms/cm ³
D	Diffusion coefficient for fission product migration in coating, cm ² /sec
D^*	Apparent diffusion coefficient obtained using $D^*t/\ell^2 = 1/6$, cm ² /sec
D_k	Diffusion coefficient for fission product migration in kernel, cm ² /sec
E	Neutron energy, meV
FIMA	Fissions in metal atoms
FR	Fraction of total fission product released, no units
h'	Film coefficient for mass transfer, cm/sec
HTGR	High-Temperature Gas-Cooled Reactor
HTI	Isotropic pyrocarbon deposited at high temperature
ℓ	Coating thickness, $b - a$, cm
L	Correlation parameter, $3b/a^2\phi$, for depleting systems, no units
LTI	Isotropic pyrocarbon deposited at low temperature
m	Slope of experimental FR-vs-t plot, (sec) ⁻¹
M_1^0	Initial amount of fission product in source region, atoms
$N(t)$	Cumulative release from coated particle as function of time, atoms
PyC	Pyrolytic carbon
γ_k	Kernel radius, cm
t	Postirradiation annealing time, hr or sec
TRISO	Three- or four-layered coating similar to BISO coating but with added high-density SiC layer
t_o	Experimental breakthrough time, hr or sec
T	Annealing temperature, °K
V	Correlation parameter, $4\pi ab\ell$, cm ³
ϕ	Partition coefficient, $C_1^*(t)/C_2(a,t)$, no units

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11. APPENDIX A: MATHEMATICAL REPRESENTATION OF THE RELEASE OF METALLIC FISSION PRODUCTS

This appendix summarizes the mathematical representation of metallic fission product release discussed by Evans and Morgan¹ in the companion report.

For our purposes, the kernel and coating have been "smeared together" to make a single source region whose properties are such that diffusion within the source region is rapid. However, some atoms are capable of becoming permanently trapped. While we recognize that control of release by diffusion in the kernel will need to be considered for the less-volatile metallic fission products, cesium, our most important isotope, is apparently uniformly distributed in and rapidly released from the kernel at 1300°C.⁵³ Similar results have often been obtained for gases.⁵⁴ The coating is represented as a homogeneous isotopic solid in which fission products have a finite solubility.⁵⁵ Transport properties are accepted as being sensitive to structural factors and hence radiation damage; this sensitivity is greatest for those metals with only modest affinities for carbon (i.e., silver and cesium).

Linear partition coefficients are used to relate concentrations in adjacent phases. Finally, the macroscopic geometry has sometimes been represented in slab form for simplicity. Computer codes developed by others^{3,4} are available to solve problems with more complex initial and boundary conditions.

The reader wishing to pursue the mechanistic representation of metal diffusion in pyrocarbon and other graphites is referred to articles by Hammond,⁵⁶ Wolfe et al.,⁵⁷ Grove,⁵⁸ and deBoer.⁵⁹

In discussing metal transport through pyrocarbon, it is important to know that the dominant characteristics which distinguish it from gas transport are as follows:

- (1) Extreme sensitivity to temperature; for example, activation energies from 30,000 to 100,000 cal deg⁻¹ mole⁻¹ have been observed (~ 3000 cal deg⁻¹ mole⁻¹ is typical of gas transport by diffusive flow).

- (2) The capability of metals for permeating pyrocarbons having no interconnected porosity accessible to even helium, which implies utilization of a strong metal-carbon interaction.
- (3) The dependence of the diffusion coefficient on concentration above some limiting value.
- (4) The range of transport coefficients for different fission product metals; for example, pyrocarbon is effectively transparent to strontium above 1100°C, whereas zirconium is immobile at > 1500°C.

The simplest solution to Fick's second law for a long-lived species diffusing through a spherical shell is obtained when the driving potential is constant.

For the initial condition that the concentration between a and b is zero and the boundary conditions that $C(a)$ is constant and $C_b = 0$ at all times, we have from Crank:¹⁵

$$\frac{N(t)}{VC_2(a)} = \frac{Dt}{\ell^2} - \frac{1}{6} - \frac{\pi^2}{2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-\pi^2 n^2 Dt / \ell^2}, \quad (A.1)$$

where $N(t)$ is the amount of fission product released from the coated particle, V is a correlation parameter ($= 4\pi ab\ell$), $C_2(a)$ is the concentration of fission product at a , t is the annealing time, and ℓ is the coating thickness ($= b - a$). The summation on the right-hand side of Eq. (A.1) approaches zero as t increases, leaving a linear relation from which we obtain:

$$D = \ell^2 / 6t_0, \quad (A.2)$$

where t_0 is the intercept of the linear relation at $N(t) = 0$ (from Crank¹⁵).

For practical use, expressions equivalent to $N(t)/VC_2(a)$ and Dt/ℓ^2 in terms of release curve parameters are needed. It can be shown that, for constant-potential conditions,

$$N(t)/VC_2(a) = FR/6t_0 m \quad (A.3)$$

and

$$Dt/\ell^2 = t/6t_o, \quad (A.4)$$

where m is the slope of a plot of the fractional release, FR, vs time after steady state has been established.

Equation (A.3) is obtained as follows:

$$m = \Delta FR / \Delta t. \quad (A.5)$$

Substituting the definition of $FR = N(t)/M_1^0$ for FR gives:

$$m = \frac{\Delta N(t)}{\Delta t M_1^0}. \quad (A.6)$$

At steady state, Eq. (A.1) becomes

$$\frac{N(t)}{VC_2(a)} = Dt/\ell^2, \quad (A.7)$$

$$m = DVC_2(a)/M_1^0 \ell^2,$$

and by using the relationship $D = \ell^2/6t_o$,

$$C_2(a) = 6t_o M_1^0 m / V. \quad (A.8)$$

Substituting for C_2 and FR into the left-hand side of Eq. (1) now yields

$$\frac{N(t)}{VC_2(a)} = \frac{FR}{6t_o m} = \frac{t}{6t_o} - \frac{1}{6} - \frac{\pi^2}{2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-\pi^2 n^2 t/6t_o}, \quad (A.9)$$

which can be conveniently used to normalize fractional release data from different experiments and to confirm the consistency of the release mechanism, by plotting $FR/6t_o m$ vs $t/6t_o$.

D is obtained from

$$D = \frac{\ell^2}{6t_o}$$

and $C_2(a)$, which is proportional to the constant driving potential, is obtained from Eq. (A.8). Values of D and $C_2(a)$ are tabulated for each

experiment in Sect. 4; $FR(t)$ and t are given in Appendix B.

A constant driving potential can arise in a number of ways. For example, the solubility of metals in the pyrocarbon coating may be exceeded; the saturation vapor pressure of the metal may be exceeded, resulting in a two-phase system; or compounds with other fission products and/or the original kernel material may form.

Failure to meet these boundary conditions requires more complex solutions involving additional parameters. While some of these solutions are given in ref. 1, it is appropriate to discuss the consequences of an unrecognized departure from a constant-potential situation, since values of the additional parameters required, namely, the partition coefficients of metal between kernel and coating and the fraction trapped in the kernel are not available. Their determination requires either prolonged experiments to define the entire release curve or the determination of radial concentration profiles in the coating following annealing.

It was found that for a slab, the intercept of the initial slope of release-vs- Dt/ℓ^2 curves for depleting potential diffusion would give values of Dt/ℓ^2 between 0.04 and 0.16 for values of L between ∞ and 0.2, where $L = 3b/a^2\phi$, $\phi = C_1^*(t)/C_2(a,t)$, and $C_1^*(t)$ is the active source concentration or the total source concentration, $C_1(t)$, minus the trapped cesium. Preliminary calculations for L for the coated particles used in this study have narrowed the range of Dt_0/ℓ^2 to between 0.06 and 0.14. The constant-potential intercept gives a value for Dt_0/ℓ^2 of 0.167; therefore, if the constant-potential relation is used for obtaining D where a depleting potential is controlling the diffusion, the D calculated will be high by a factor of 1.2 to 3.

The effects of a film or evaporation resistance at the external surface on release were also investigated. It was found that such effects could not be detected from release data; the film coefficient would simply combine with the diffusion coefficient to give an apparent diffusion coefficient. The apparent diffusion coefficient, however, could be much lower than the actual diffusion coefficient. The relation between t_0 , D , and h' is:

$$\frac{Dt_o}{\ell^2} = \frac{1}{6} \frac{\ell h' + 3D}{\ell h' + D},$$

where h' is the film coefficient (cm/sec). If $\ell h'$ were to approach D in magnitude, the apparent D calculated from t_o would be low by a factor of about 3. As h' approaches infinity, the film resistance is negligible and the calculated D will be a true value. In order to determine film effects, concentration profiles of the coatings must be obtained. In application of the coefficients to calculations of release, the apparent D may be used to obtain the same result. However, if the film coefficient changes differently with temperature than does D , the calculated activation energy will be affected and extrapolation of the apparent D to other temperatures may not be valid.

Finally, the situation in which diffusion in the kernel is not rapid must be discussed briefly. In the limit where $D_k \ll D$ and the kernel is controlling release, the later part of the fractional release curve will tend to have a constant slope (characteristic of diffusion from a sphere with diffusion coefficient D_k) when FR is plotted against $t^{1/2}$. While removal of the coating from the kernel before annealing yields a more rapid determination of D_k , the reactivity of the kernel toward air and water makes prolonged annealing of the integral coated particle an acceptable alternative at higher temperatures. This method was used by Langer⁶⁰ to determine kernel coefficients for strontium. Flowers and Brown⁶¹ have utilized the impermeability of SiC to metals to collect metals released from large oxide kernels in the buffer and inner pyro-carbon coatings of intact fuels containing SiC coatings.

12. APPENDIX B: TABLES OF FRACTIONAL FISSION PRODUCT RELEASE
DURING POSTIRRADIATION ANNEALS

The tables included in this appendix contain the experimental release-vs-time data obtained during the study reported here. The tables are arranged by type of coated particle and annealing temperature, starting with Group A.

Table B-1. Cesium release from lower-burnup Group A particles during postirradiation anneals at 1250°C

Group A particles: LTI-PyC-coated UO_2 , 11% FIMA

A-1		A-2		A-3 ^a		A-4 ^a	
t (hr)	FR (%)	t (hr)	FR (%)	t (hr)	FR (%)	t (hr)	FR (%)
232	0.0006	232	0.0001	213	<0.017	756	0.018
444	0.002	444	0.0059	642	0.0315	847	0.019
657	0.008	657	0.1025	846	0.240	1087	0.097
914	0.035	914	0.585	1110	0.600	1328	0.214
1178	0.066	1178	0.960			1598	0.592
1416	0.165	1416	1.217			1834	0.919
1626	0.300	1626	1.652				

^aA-3 and A-4 are fuel pellets.

Table B-2. Cesium release from lower-burnup Group A particles during postirradiation anneals at 1400°C

Group A particles: LTI-PyC-coated UO_2 , 11% FIMA

A-5 ^a		A-6		A-7		A-8	
t (hr)	FR (%)	t (hr)	FR (%)	t (hr)	FR (%)	t (hr)	FR (%)
15	0.00075	6	0.004	9.60	0.004	24	0.003
19	0.00325	12	0.013	15.00	0.080	30	0.013
23	0.00975	18	0.114	18.00	0.153	36	0.043
27	0.02550	24	0.374	24.00	0.358	42	0.076
31	0.05475	30	0.779	40.00	1.24	48	0.131
35	0.132	36	1.176	89.00	5.88	54	0.214
191	6.13	42	2.118			71.5	0.541
		60	3.576			90	1.102
		84	5.025			107	1.855
		108	6.072			123	2.96
		130	9.345			141	3.45
		152	14.584			159	4.22
		176	16.705			177	5.55

A-9		A-10		A-11		A-12	
t (hr)	FR (%)	t (hr)	FR (%)	t (hr)	FR (%)	t (hr)	FR (%)
24	1.91	24	2.58	24	0.23	24	0.21
30	3.24	30	4.04	30	0.44	30	0.62
36	6.03	36	5.89	36	0.92	36	1.78
42	8.12	42	7.79	42	1.28	42	2.96
48	9.88	48	9.19	48	1.56	48	3.81
72	14.97	72	17.37	72	2.64	72	7.33
96	18.60	96	22.38	96	4.05	96	10.72

^aA-5 is an average of four coated particles.

Table B-3. Cesium release from lower-burnup Group A particles during postirradiation anneals at 1500°C

Group A particles: LTI-PyC-coated UO_2 , 11% FIMA

t (hr)	Fractional release (%)							
	A-13	A-14	A-15	A-16	A-17	A-18	A-19	A-20
1	0.0039	0.0068	0.0033	0.0042	0.0027	0.0048	0.0034	0.0031
2	0.0023	0.0135	0.0025	0.0062	0.0252	0.0016	0.0036	0.0735
3	0.0430	0.203	0.0028	0.0992	0.899	1.362	0.639	0.747
4	0.5650	2.222	0.0194	0.645	3.599	3.701	2.194	2.484
5	1.91	4.42	0.0701	1.42	7.38	5.75	4.29	4.37
6	3.49	7.18	0.158	2.40	11.13	7.74	6.55	6.61

Table B-4. Cesium release from lower-burnup Group A particles during postirradiation anneals at 1600°C

Group A particles: LTI-PyC-coated UO_2 , 11% FIMA

t (hr)	Fractional Release (%)							
	A-21	A-22	A-23	A-24	A-25	A-26	A-27	A-28 ^a
1	0.62	0.89	0.22	0.45	1.90	0.62	1.53	0.017
2	5.96	9.17	4.67	5.70	9.54	5.05	10.66	0.454
3	11.4	16.3	9.98	13.5	15.6	9.45	17.69	1.69
4	16.8	20.8	14.7	19.7	22.1	13.9	22.5	3.23
5								5.15

^aA-28 is a group of four coated particles.

Table B-5. Cesium release from higher-burnup Group A particles during postirradiation anneals at 1250°C

Group A particles: LTI-PyC-coated UO_2 , 22% FIMA

A-29 ^a		A-30 ^a		A-31	
t (hr)	FR (%)	t (hr)	FR (%)	t (hr)	FR (%)
270	0.06	170	0.007	232	0.017
583	2.6	379	1.47	444	4.26
974	8.1	592	5.23	657	10.19
1286	11.7	812	8.11	914	14.37
1624	16.6	1020	10.73	1178	17.27
2002	20.1			1416	18.05
2503	24.3			1626	20.33
2700	28.9				
2800	30.0				

^aA-29 and A-30 are miniature fuel sticks.

Table B-6. Cesium release from higher-burnup Group A particles during postirradiation anneals at 1400°C

Group A particles: LTI-PyC-coated UO_2 , 22% FIMA

t (hr)	Fractional release (%)			
	A-32	A-33	A-34	A-35
12	7E-4	5E-4	-	5E-4
15	7E-4	0.011	2E-3	6E-3
19	-	0.108	8E-3	0.05
23	3E-3	0.286	0.015	0.114
27	0.023	0.688	0.029	0.257
31	0.11	1.14	0.065	0.428
35	0.264	1.48	0.096	0.580
191	14.25	9.09	3.75	5.65

Table B-7. Cesium release from higher-burnup Group A particles during postirradiation anneals at 1600°C

Group A particles: LTI-PyC-coated UO_2 , 22% FIMA

A-36	t(hr)	1	2	3	4	5
	FR(%)	0.111	1.46	3.73	6.18	8.44

Table B-8. Cesium release from Group B particles during postirradiation anneals at 1600°C

Group B particles: LTI-PyC-coated UO_2 , 13% FIMA

B1	t(hr)	3	6	9	12	18
	FR(%)	0.32	0.48	1.06	2.81	7.46
B2	t(hr)	3	6	9	12	18
	FR(%)	0.96	1.04	1.54	2.83	7.03

Table B-9. Cesium release from Group C particles during postirradiation anneals at 1400°C

Group C particles: LTI-PyC-coated ThO₂, 3.5% FIMA

t (hr)	C-1 FR (%)	C-2 FR (%)	C-3 FR (%)	C-4 FR (%)
104	0.012	0.010	0.014	0.015
128	0.019	0.015	0.021	0.020
152	0.034	0.024	0.020	0.056
176	0.061	0.045	0.053	0.080
200	0.086	0.060	0.077	0.112
224	0.120	0.086	0.099	0.139
248	0.137	0.099	0.130	0.170
272	0.164	0.126	0.178	0.210
296	0.198	0.149	0.203	0.232
320	0.223	0.170	0.231	0.279
344	0.226	0.200	0.283	0.329
433	0.399	0.310	0.425	0.482
506	0.482	0.364	0.543	0.599
596	0.647	0.505	0.717	0.742
780	0.926	0.770	1.05	1.05
953	0.990	0.976	1.27	1.27
1093	1.30	1.18	1.51	1.53
1237	1.98	1.42	1.73	1.77
1397	3.21	1.58	1.96	2.00
1554	4.64	1.76	2.10	2.17
1714	7.27	1.93	2.29	2.32
1860	8.66	2.02	2.34	2.42
1934	9.94	2.09	2.43	2.45
2056	13.10	2.19	2.58	2.60
2144	13.59	2.15	2.66	2.62
2280	18.37	2.38	2.79	2.90
2441	21.05	2.55	3.02	3.09
2601	24.19	2.61	3.15	3.11
2713	26.39	2.70	3.18	3.22
2848	29.18	2.76	3.29	3.36
3024	34.78	2.89	3.42	3.63
3155	35.80	2.90	3.54	3.61
3315	39.08	2.95	3.63	3.87
3472	41.30	2.95	3.66	3.99
3597	--	2.93	3.83	4.22
3630	42.97	--	--	--
3755	--	3.04	3.96	4.42

Table B-10. Cesium release from Group C particles during postirradiation anneals at 1600°C

Group C particles: LTI-PyC-coated ThO_2 , 3.5% FIMA

t (hr)	C-5 FR (%)	C-6 FR (%)
9	0.011	0.012
14	0.073	0.071
19	0.208	0.192
24	0.357	0.307
29	0.532	0.444
34	0.709	0.585
39	0.909	0.739
44	1.17	0.955
60	1.78	1.61
76	2.63	2.97
92	3.86	6.59
114	9.45	14.54
132	19.9	19.80
156	39.2	29.8
186	50.7	36.3
210	54.5	43.3
234	58.0	50.4
259	65.7	54.1
282	66.4	59.3
317	70.4	63.2
365	72.2	67.0
408	75.0	67.4
451	77.4	71.6
499	78.8	69.0
592	80.8	71.2
661	81.5	71.2
781	82.3	71.8

Table B-11. Cesium release from Group D particles during postirradiation anneals at 1400°C

Group D particles: LTI-PyC-coated UC₂, 13% FIMA

t (hr)	D-1 FR (%)	D-2 FR (%)	D-3 FR (%)
98	0.21	0.54	0.31
118	0.19	0.36	0.28
136	0.41	0.76	0.53
156	0.90	1.03	0.45
172	0.60	1.53	0.64
220	0.90	2.35	1.07
262	1.25	3.18	1.42
302	1.56	4.07	1.83

Table B-12. Cesium release from Group D particles during postirradiation anneals at 1600°C

Group D particles: LTI-PyC-coated UC₂, 13% FIMA

t (hr)	D-4 FR (%)	D-5 FR (%)
6	0.40	0.39
9	1.27	0.82
12	2.35	1.75
18	4.44	3.73

Table B-13. Cesium release from Group E particles during postirradiation anneals at 1400°C

Group E particles: HTI-PyC-coated UC₂, 13% FIMA

t (hr)	E-1 FR (%)	E-2 FR (%)	E-3 FR (%)
98	0.56	0.25	0.22
118	0.89	0.62	0.66
136	0.98	0.47	0.39
156	1.25	1.19	0.62
172	1.52	1.63	1.04
220	2.14	2.19	1.55
262	2.97	3.17	2.12
302	3.48	4.05	2.66

Table B-14. Cesium release from Group E particles during postirradiation anneals at 1600°C

Group E particles: HTI-PyC-coated UC₂, 13% FIMA

t (hr)	E-4 FR (%)	E-5 FR (%)
6	0.48	0.67
9	2.65	3.22
12	6.34	6.45
18	14.57	14.35

Table B-15. Cesium release from Group F particles during postirradiation anneals at 1400°C

Group F particles: HTI-PyC-coated ThO₂, 3.5% FIMA

t (hr)	F-1 FR (%)	F-2 FR (%)	F-3 FR (%)	F-4 FR (%)
1237	--	--	--	0.0054
1397	--	--	--	0.0099
1554	0.0004	0.0004	0.0000	0.0126
1714	0.0016	0.0016	0.0016	0.0138
1860	0.0028	0.0024	0.0023	0.0199
1934	0.0044	0.0033	0.0086	0.0249
2056	0.0298	0.0135	0.0250	0.0398
2144	0.0286	0.0086	0.0211	0.0421
2280	0.0306	0.0090	0.0227	0.0486
2441	0.0346	0.0119	0.0250	0.0552
2601	0.0373	0.0127	0.0266	0.0659
2713	0.0397	0.0144	0.0297	0.0724
2848	0.0417	0.0135	0.0344	0.0816
3024	0.0469	0.0172	0.0379	0.0969
3155	0.0477	0.0131	0.0414	0.1053
3315	0.0536	0.0160	0.0489	0.1107
3440	0.0588	0.0197	0.0524	0.1172
3597	0.0643	0.0230	0.0547	0.1241
3755	0.0707	0.0308	0.0629	0.1379

Table B-16. Cesium release from Group F particles during postirradiation anneals at 1600°C

Group F particles: HTI-PyC-coated ThO₂, 3.5% FIMA

t (hr)	F-5 FR (%)	F-6 FR (%)
132	0.0060	0.0020
156	0.0142	0.0043
186	0.0249	0.0053
210	0.0556	0.0112
234	0.0858	0.0319
259	0.1120	0.0452
282	0.1430	0.0668
317	0.2640	0.1170
365	0.4250	0.2000
408	0.5130	0.2790
451	0.7310	0.3980
499	0.8630	0.4770
592	1.170	0.6850
661	1.380	0.7870
781	1.860	1.1600

Table B-17. Cesium release from Group G particles during postirradiation anneals at 1600°C

Group G particles: HTI-PyC-coated ThO₂, 3.5% FIMA

t (hr)	G-1 FR (%)	G-2 FR (%)
365	0.0034	0.0031
408	0.0025	0.0015
451	0.0170	0.0128
499	0.0246	0.0164
592	0.0209	0.0138
661	0.0231	0.0177
781	0.0177	0.0150

Table B-18. Cesium release from Group H particles during postirradiation anneals at 1600°C

Group H particles: HTI-PyC-coated ThO₂, 3.5% FIMA

t (hr)	H-1 FR (%)	H-2 FR (%)
92	0.225	0.292
114	0.574	0.600
132	0.901	0.880
156	1.38	1.38
186	1.91	1.76
210	2.52	2.37
234	3.27	3.27
259	3.99	3.89
282	4.67	4.70
317	6.03	5.69
365	7.51	7.08
408	8.75	--
451	9.66	--
499	10.86	9.14
592	12.55	11.11
661	15.21	12.81
781	17.71	14.68

Table B-19. Strontium and barium release from Group A particles during postirradiation anneals at 1500°C

Group A particles: LTI-PyC-coated UO_2 , neutron activated

t (hr)	A-37		A-38		A-39		A-40		A-41	
	Sr FR (%)	Ba FR (%)	Sr FR (%)	Ba FR (%)	Sr FR (%)	Ba FR (%)	Sr FR (%)	Ba FR (%)	Sr FR (%)	Ba FR (%)
5	0.05	0	0.01	0.02	0.45	0.01	0.30	0.01	0.45	0.02
10									0.77	0.10
15	0.37	0.06	0.48	0.25	0.91	.15	0.59	0.18		
20									1.02	0.28
30	0.97	0.59					0.80	0.74		
32					6.05	1.18				
35			21.42	12.29						
36							1.05	1.24		
40									1.35	0.61
41							2.59	1.70		
46							5.30	2.56		
51							7.90	5.78		
56							10.26	12.51		
60	3.42	2.10	22.24	16.91	14.11	8.39				
66							12.49	17.88		
70									1.78	1.04
120	28.44	14.19	22.62	42.75	15.21	20.44			2.21	1.50
180	28.84	23.95	22.64	52.75	15.53	31.23			2.66	1.84

Table B-20. Strontium and barium release from Group A particles during postirradiation anneals at 1700°C

Group A particles: LTI-PyC-coated UO_2 , neutron activated

t (hr)	A-42		A-43		A-44		A-45	
	Sr	Ba	Sr	Ba	Sr	Ba	Sr	Ba
	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)
5			0.102	0.02	0.094	0.061	0.0807	0.0234
10			0.136	0.07	0.136	0.128	0.1350	0.1791
15			0.164	0.139	0.173	0.173	0.1446	0.3757
20			0.188	0.199	0.212	0.218	0.1454	0.4424
25			0.221	0.251	0.231	0.257	0.1463	0.4871
30							0.1467	0.5018
35					0.276	0.319		
40			0.309	0.357			0.1482	0.5214
45					0.307	0.378		
50							0.1490	0.5277
70							0.1507	0.5311
75					0.356	0.498		
80			0.418	0.512				
120					0.372	0.589		
180	0.65	0.629	0.658	0.673	0.394	0.651		
360	0.79	0.812						
540	0.84	0.882						

Table B-21. Cerium and barium release from Group D particles during postirradiation anneals at 1150°C

Group D particles: LTI-PyC-coated UC₂, 13% FIMA

t (hr)	D-6		D-7		D-8		D-9	
	Ce	Ba	Ce	Ba	Ce	Ba	Ce	Ba
	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)
2		1.17		1.00		2.31		3.37
3		1.17		7.46		7.04		4.73
4		5.00	0.0365	10.20		7.08		4.96
5	0.0213	5.84	0.0803	12.50	0.262	12.00	0.310	11.30
6	0.00834	11.10	0.0554	18.00	0.384	13.10	0.507	17.60
7	0.0333	12.90	0.115	15.20	0.686	16.20	1.38	25.30
8	0.0416	14.00	0.117	15.30	0.688	16.30	1.39	25.40
9	0.0715	16.60	1.34	16.30	1.23	17.40	1.39	25.60
10	0.0962	18.90	7.20	16.20	1.40	17.40	1.39	26.00
11	0.114	20.50	7.70	17.30	2.45	17.60	1.39	26.30
12	0.178	22.40	8.24	18.10	2.46	17.70	1.39	26.40
18	2.69	25.20	8.24	—	2.59	23.90	5.79	38.70
34	2.74	25.60	9.62	19.7	10.10	—	6.29	39.00
39	5.47	25.50	12.50	19.7	10.10	24.00	6.30	39.00
55	5.49	26.4	12.50	—	12.20	—	13.80	—
71	10.50	—	16.60	—	12.30	—	13.80	—

Table B-22. Cerium release from Group D particles during postirradiation anneals at 1400°C

Group D particles: LTI-PyC-coated UC₂, 13% FIMA

t (hr)	D-10 FR (%)	D-1 FR (%)	D-2 FR (%)	D-3 FR (%)
10	52.1	51.1	50.4	45.7
16	68.8	63.5	65.2	58.6
22	79.0	69.8	72.5	62.2
28	82.2	71.8	73.9	63.8
44	85.2	76.9	78.1	64.2
62	86.6	77.5	80.4	65.6
80	87.5	80.8	80.8	65.4

Table B-23. Cerium and barium release from Group E particles during postirradiation anneals at 1150°C

Group E particles: HTI-PyC-coated UC₂, 13% FIMA

t (hr)	E-6		E-7		E-8		E-9	
	Ce	Ba	Ce	Ba	Ce	Ba	Ce	Ba
	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)	FR (%)
5		0.172				0.21		0.13
6		0.134		0.139		0.38		0.50
7		0.263		0.190		1.50		0.51
8		0.263		0.190		1.58		0.73
9		0.907		0.950		2.12		1.89
10		1.63		1.78		2.75		2.07
11		2.37		1.99		2.83		2.80
12		3.04		2.96		3.82		5.06
18		9.12		8.89		10.20		8.76
34	0.214	15.30	0.0235	20.80	0.0219	14.40	0.781	21.30
39	0.218	15.80	0.0309	21.60	0.0381	15.50	0.792	21.80
55	0.462	21.00	2.13		0.837		1.54	
71	0.520						1.63	

Table B-24. Cerium release from Group E particles during postirradiation anneals at 1400°C

Group E particles: HTI-PyC-coated UC₂, 13% FIMA

t (hr)	E-1 FR (%)	E-10 FR (%)	E-2 FR (%)	E-3 FR (%)
10	65.6	61.5	66.7	48.3
16	77.7	73.9	81.4	66.9
22	84.5	80.8	86.5	76.9
28	86.8	84.3	91.5	82.9
44	90.9	86.2	95.8	89.8
62	92.8	87.8	97.9	94.7
80	92.1	88.8	96.8	94.2

13. APPENDIX C: CHARACTERIZATION, PROPERTIES, AND HISTORY OF MATERIALS USED

The coating deposition conditions, preirradiation characteristics, and irradiation histories of the coated particles used in the annealing experiments are given in Tables C-1, C-2, and C-3. Details not previously covered in Sect. 3 are described below.

13.1 Description of Irradiation Experiments

13.1.1 Irradiation experiments B9-41 and B9-42 (Group A particles)

The Group A coated particles were irradiated in two identical capsules, both as particles in a loose bed and as particles bonded in fuel pellets, in two successive irradiations (B9-41 and B9-42) to 22% and 11% FIMA, respectively, in the ORR. Each irradiation capsule contained 15 fuel samples in graphite cans. Of the 15 cans in each irradiation experiment, 7 contained fuel pellets with TRISO-coated particles, 6 contained fuel pellets with BISO-coated particles, and 2 were filled with loose coated particles in graphite powder (1 can of TRISO-coated particles and 1 can of BISO-coated particles). Only the Group A samples with BISO coatings were used in the diffusion anneal experiments. Irradiation data are given in Table C-1. Other details of the irradiation are given in ref. 40.

13.1.2 Irradiation experiment C1-28 (Groups B, D, and E particles)

Groups B, D, and E coated particles were irradiated to 13% FIMA in the C1-28 irradiation experiment. This experiment contained 21 different types of coated particles arranged symmetrically around bonded fuel elements.⁴¹ The purposes of the experiment were to test resin-based fissile particles in intrusion bonded beds under large temperature gradients and at high temperatures and to irradiate a selection of coated particles, both of conventional and advanced design, for use in fission product annealing studies.

A large number of coated particles failed at the beginning of irradiation, presumably as a result of thermal cycling and differential expansion between the coated particles and the fuel tubes during irradiation. Although the temperature of the graphite sleeve of the capsule was generally less

Table C-1. Characteristics and irradiation history of
Group A coated particles, ORNL Batch No. OR10105B

Coating Deposition Conditions and Characteristics				
Layer	Buffer	Outer	SACL 1	SACL 2
Type	Porous	High-density, isotropic	High-density, nonbonding, anisotropic	High-density, bonding, isotropic
Hydrocarbon	C ₂ H ₂	C ₃ H ₆	C ₃ H ₆	C ₃ H ₆
Supply rate, cc/cm ² ·min	4.8	3.4	0.11	2.3
Deposition temp., °C	1050	1250	1100	1300
Deposition rate, μm/min	24	7.7	~0.2	10
Coating thickness, μm	41	64	~5	13
Coating density, g/cm ³	-	2.01	-	-
Average Preirradiation Conditions				
Uranium content, wt %	39.1			
Carbon content, wt %	55.6			
Uranium enrichment, at. %	97.68			
Coated particle OD, μm - avg.	482			
- standard dev.	24			
Kernel diameter, μm - avg.	235			
- standard dev.	12			
Kernel composition	Sol-gel UO ₂			
Total coating thickness, μm - avg.	123			
- standard dev.	9			
Coated particle density, g/cm ³	2.90			
Surface contamination, % of total U	< 0.01E-3			
After first leach, % of total U	< 0.01E-3			
Fuel removal during leach, % of total U	< 0.03E-3			
Irradiation History				
Reactor	ORR - B9 Core Position			
Irradiation temp., °C	< 700			
Neutron flux φ _{th} , neutrons/cm ² ·sec	4E13			
Time at power, sec				
Burnup = 11% FIMA	5.0E6			
Burnup = 22% FIMA	8.9E6			
Neutron flux ratios for B-9 facility:				
φ _r = 0.1 φ _{th}				
φ > 0.18 MeV = 0.7 φ _{th}				
φ > 0.7 MeV = 0.5 φ _{th}				
φ > 2.9 MeV = 0.15 φ _{th}				

Table C-2. Characteristics and irradiation history of Groups B, D, and E coated particles^a

Group	Batch	Type	Coated-particle preirradiation characteristics						Source gas
			Kernel diameter (μm)	Buffer		Outer isotropic coating		OPTAF	
				Thickness (μm)	Density (g/cm ³)	Thickness (μm)	Density (g/cm ³)		
B	4413-35E	UO ₂ -LTI	114	57	1.23	57	1.85	1.00	Propane
D	4403-81E	UC ₂ -LTI	108	56	1.17	52	1.83	1.06	Propane
E	3516-47E	UC ₂ -HTI	110	62	1.23	48	1.82	1.00	Methane

Irradiation History

Reactor	ORR-C1 Core Position
Irradiation temp., °C	< 800
Neutron flux ϕ_{th} , neutrons/cm ² ·sec	3.5E13
Time at power, sec	5.9E6
Burnup, % FIMA	13
Neutron flux ratios for C-1 facility:	
$\phi_{\text{r}} = 0.1 \phi_{\text{th}}$	
$\phi > 0.18 \text{ MeV} = 0.7 \phi_{\text{th}}$	
$\phi > 0.7 \text{ MeV} = 0.5 \phi_{\text{th}}$	
$\phi > 2.9 \text{ MeV} = 0.15 \phi_{\text{th}}$	

^aThese coated particles were supplied by the General Atomic Company.

Table C-3. Characteristics and irradiation history of
Groups C, F, G, and H coated particles

Outer Coating Deposition Conditions ^a				
Group	C	F	G	H
Deposition temp., °C	1250	2000	2000	1250
Coater diameter, cm	2.54	2.54	3.5	3.5
Source gas	C ₃ H ₆	CH ₄	CH ₄	C ₃ H ₆
Partial pressure, ^b torr	760	152	63	760
Supply rate, cm ³ /min-cm ²	4.0	1.0	1.0	3
Initial bed surface area, cm ²	1750	700	1000	2000
Total flow rate, cm ³ /min	8000	3500	1200	8000
Annealing temp., °C	--	--	--	1900
Weight of ThO ₂ particle charge, g	55	22	43	87
Coated Particle Characteristics ^c				
Group	C	F	G	H
Outer coating:				
Density, g/cm ³	2.00	1.81	2.01	2.04
Bacon anisotropy factor	1 ^d	1.1 ^e	~1.3 ^e	~1 ^e
L _C , apparent cryst. size, Å	30 ^f	110 ^f	~120	~120
Average thickness, μm	75	75	150	150
Buffer layer thickness, μm	40 ^g	40	100 ^g	100 ^g
Kernel diameter, μm	275	275	425	425
Calculated postirradiation outer coating density, μm	2.05	1.95	2.05	2.07
Irradiation History				
Reactor	HFIR - F7 target position			
Irradiation temp., °C	650			
Time at full power of 100 MW, sec	5.72 x 10 ⁶			
Burnup, % FIMA	3.5			
Fast-neutron dose, E > 0.18 MeV, neutrons/cm ²	4 x 10 ²¹			

^aThe coated particles and deposition conditions were obtained from D. M. Hewette of the ORNL Metals and Ceramics Division.

^bThe system exhaust was at atmospheric pressure, and helium was used as a diluent when needed.

^cPreirradiation characteristics were obtained from ref. 44.

^dDetermined by x-ray diffraction for coatings stripped from disks.

^eEstimated from structural appearance and deposition conditions.

^fApparent crystallite sizes were determined by (002) line broadening.

^gThe buffer layer was sealed.

than 800°C, cesium was found to be distributed throughout the capsule. Irradiation data are given in Table C-2.

13.1.3 Irradiation experiment HT-1 (Groups C, F, G, and H particles)

Groups C, F, G, and H coated particles were irradiated in the F-7 target position of the HFIR. The purpose of this irradiation experiment was to study the effects of fast-neutron irradiation on the integrity and dimensional behavior of fuel pellets containing coated particles. Loose BISO-coated ThO₂ particles and pyrolytic-carbon strip specimens were included in the study to permit the effects of coating properties on irradiation-induced density and dimensional changes of pyrocarbon to be determined.⁴² Results of postirradiation examinations are given in refs. 29, 44, 45, and 46.

Preirradiation and postirradiation densities of pyrolytic-carbon-coated strips, coated simultaneously with the particles and irradiated in the same experiment, were compared with those of the particle coatings.^{28,29} Densification in the particle coatings was determined from dimensional changes, while that in the carbon strips was obtained by measuring the densities of the strips before and after irradiation with a density gradient technique. There was considerable scatter in the limited data; and, although variations in densification as a function of coating type and crystallite size are indicated in the data from material irradiated to 6×10^{21} neutrons/cm² ($E > \text{MeV}$) at 1100°C, there is hardly any such distinction in the data from samples irradiated at 650°C to a fast fluence of 4×10^{21} neutrons/cm² ($E > 0.18 \text{ MeV}$). These data include densification information for equivalent or identical structures of coated particles used in Group C, F, G, and H annealing studies. Since the coated particle densification was not biased relative to the carbon strip values, all the 650°C data were used even though agreement was not good. A least-squares fit of this data gave the relation

$$\Delta P/P_0 = 0.570 - 0.273 P_0$$

This relation was used to calculate the postirradiation densities of the Group C, F, G, and H coated particles (Table C-3).

Postirradiation values of crystallite size and anisotropy were not determined. According to Bokros,⁶² the apparent crystallite size, L_c , would be expected to increase during fast-neutron irradiation if the original L_c values were less than 50 Å, and decrease if the original values were more than 50 Å, for pyrocarbons irradiated to 1000°C to a fast-neutron fluence of $\sim 2 \times 10^{21}$ neutrons/cm² ($E > 0.18$ MeV). The anisotropy of coatings of YZ-134 (Group C) particles was observed by Hewette⁶³ using polarized light microscopy to increase significantly, while that of coatings of YZ-135 (Group F) particles increased only slightly (if any), in another irradiation experiment at 1275°C to a fast-neutron fluence of 5×10^{21} neutrons/cm² ($E > 0.18$ MeV).

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