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DEVELOPMENT OF FUELED GRAPHITE CONTAINING PYROLYTIC-CARBON COATED
CARBIDE PARTICLES FOR NONPURGED, GAS-COOLED REACTOR SYSTEMS

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ABSTRACT

Progress is reported in several areas of development of fueled graphite containing coated particles for nonpurged gas-cooled reactor systems. The sol-gel process has been modified for making spherical particles of both thorium-uranium carbide and thorium-uranium oxide suitable for coating. Equipment has been assembled and methods have been developed for deposition of pyrolytic-carbon coatings under well-controlled conditions. Damage to coated particles during fabrication into a graphite matrix depends on the molding pressure and the volumetric content of coated particles. Vendor-supplied coated particles and fueled graphite spheres have been evaluated extensively in both in- and out-of-reactor tests. Duplex- and triplex-coated particles have excellent fission-gas retention at 2050°F to burnups of 15 at. %, and one triplex sample has also shown good retention at 2500°F to 20 at. % burnup. Fueled graphite spheres containing coated particles have good irradiation performance, but the fission-gas release rates are somewhat higher than for unsupported coated particles. Fueled graphite spheres react with water vapor about as rapidly as do Speer Mod-2 and ATJ grades of graphite. The diffusion rates in pyrolytic carbon are the same for uranium, thorium, and protactinium. The diffusion rates in the direction parallel to the deposition plane are much higher than those in the perpendicular direction.

INTRODUCTION

The coated-particle fuels program at the Oak Ridge National Laboratory is concerned with the development of fueled-graphite elements for non-purged, gas-cooled power reactor systems, principally of the pebble-bed type. The program includes fuel-particle preparation studies, pyrolytic-carbon coating studies, fueled-graphite fabrication development, extensive in- and out-of-reactor evaluation of coated-particle materials including vendor-supplied specimens, studies of the compatibility of fueled graphite with water vapor, and studies on migration of uranium, thorium and protactinium in pyrolytic carbon.

This paper describes the techniques used and the significant results and implications that have evolved in the ORNL Coated-Particle Fuels Program.

MATERIALS PREPARATION

Particle Preparation
(O. C. Dean, Chemical Technology Division)

The sol-gel process (1, 2, 3) developed at ORNL to prepare oxide fuels suitable for vibratory compaction has been adapted to the preparation of spheres of oxides and carbides of thorium or thorium-uranium. This technique promises to provide a simple low-cost procedure for preparing spherical fuel particles suitable for fueled graphite and other fueled matrices.

In four simple steps thorium nitrate and uranyl nitrate are converted to spheres of thorium oxide or thorium-uranium oxide which have particle densities greater than 99% of the theoretical crystal density. The addition of one procedural step produces the carbide spheres (Fig. 1).

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- - - - ROUTE FOR CARBIDE PREPARATION

Fig. 1. Sol-Gel Process for Preparation of Dense Spheres of Uranium-Thorium Oxides or Carbides.

Thorium nitrate solution or crystals are denitrated to thorium oxide of small crystallite size and high surface area by heating in a current of superheated steam. The thoria product is readily dispersed to a stable sol by agitation with dilute nitric acid or uranyl nitrate at 80°C. Adjustment of the pH of the sol leads to a final product which is a solid solution of UO_2 in ThO_2 having a near-perfect uniformity of uranium-to-thorium ratio. To form spheres the sol, at a concentration of 4 moles of ThO_2 per liter, is sprayed into a mixture of carbon tetrachloride and isopropyl alcohol which is circulated upward in a tapered column counter-current to the falling sol droplets. The taper of the column controls the velocity of organic flow so that sufficient residence time is maintained for setting the sol drops to gels by dehydration with the alcohol. Drying is completed in air at 85°C. The spheres are densified by calcination. The temperature is raised slowly to 500°C, then rapidly to 1200°C, and fired at this temperature for 4 hr. When uranium is present, the firing is conducted at 1150°C in argon containing 4% hydrogen to produce $\text{ThO}_2\text{-UO}_2$ solid solution.

In the preparation of the carbide spheres, channel black of high surface area is dispersed in the oxide sols described above. The spheres are formed, gelled, and dried as described for the oxides. The blended oxide-carbon gel spheres are converted to carbides and sintered by heating in vacuum at 1750°C or in 1 atm of CO at approximately 2100°C for 1 hr. At these conditions, the stoichiometry may be regulated so as to give a product ranging in composition from monocarbides with only traces of dicarbide and no free carbon to a product of dicarbides containing excess free carbon and no monocarbide detectable by x-ray diffraction. Oxygen

contents on dicarbide preparations were less than 200 ppm. Densities of the dicarbides ranged from about 80 to 95% of theoretical.

Figure 2 contains a photomicrograph of thoria microspheres having a diameter of 100 to 250 μ which were prepared by the sol-gel technique as described above. They have densities greater than 9.9 g/cm³, a very low total porosity which is well-distributed as extremely small pores throughout the solid. In addition, they are very strong and tough. Microspheres of 5 wt % UO₂-95 wt % ThO₂ were prepared also and had properties almost identical with those of the ThO₂ spheres except for color.

Particle Coating Studies
(R. L. Beatty and E. S. Bomar,
Metals and Ceramics Division)

Two furnaces have been set up for the fluidized-bed application of pyrolytic-carbon coatings to -60 +100 mesh spheroidal particles of nuclear fuels and poisons. The apparatus used for initial studies is shown in Fig. 3 and is still being used for work at 1400°C and lower. It consists of a graphite tube with a 30° included-angle nozzle, supported on a water-cooled brass tube, all contained within a mullite tube. The fluidizing and carbonaceous gases are introduced through a central nozzle (opening). Heating is provided by SiC-resistance elements. Temperature is controlled by a thermocouple located outside the mullite tube and previously calibrated against a thermocouple placed in the fluidized bed.

The second furnace is heated by a graphite resistor and can be operated at temperatures to 2000°C. A cutaway view of the furnace appears in Fig. 4. This furnace also uses a 30° included-angle graphite nozzle supported on a water-cooled tube, but the gases are admitted through

Fig. 2. Thoria Microspheres Calcined at 1200°C for 4 hr. Prepared by the sol-gel technique.

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Fig. 3. Fluidized Bed Particle Coating Apparatus.

Fig. 4. High-Temperature Fluidized Bed Particle Coating Apparatus.

a central hole ($\text{CH}_4 + \text{He}$) and a concentric annulus (He or H_2). Temperature is controlled by means of an optical pyrometer, which is sighted on the graphite reaction tube through a port at the side of the furnace. This reading is calibrated against direct measurements of the temperature of the fluidized bed that can be taken through the top of the furnace when hydrocarbon gas is not flowing.

The relative position of the heating element and the gas-entrance port of the nozzle have been selected to minimize the variation in temperature in the fluidized bed. This choice was made to provide a closer control over the temperature at which the coating is applied even though it makes operation of the equipment without nozzle blockage more difficult.

Both systems are capable of operating below atmospheric pressure, and total gas pressures ranging from 100 mm Hg to atmospheric have been employed. Helium and hydrogen have served as diluent or carrier gases when needed, and the carbon was supplied as methane or acetylene.

The normal coating procedure consists of (1) heating the furnace to the desired initial coating temperature while purging with helium; (2) adjusting the carrier-gas flow to a level sufficient to fluidize the particles; (3) adding the charge of particles (5-25 g); (4) re-adjusting the gas flow rates to supply the required ratio of hydrocarbon to carrier gas; (5) continuing the run to apply the desired coating thickness; and (6) in some cases, raising the furnace temperature while fluidizing the particles with helium and continuing the run at a higher temperature. Where coatings in excess of 50- μ thickness are applied, it is sometimes necessary to reduce the gas velocity as the run proceeds to avoid throwing particles out of the reaction zone. This can be done by

reducing the carrier-gas flow rate or, in the case of subatmospheric pressure runs, by raising the system overpressure. Samples of coated particles can be removed at intervals during the run by momentarily cutting off the gas supply and allowing a few particles to fall through the nozzle into a sample receiver, which is an extension of the coating chamber but is located below the furnace.

Initial coating work was performed with -60 +80 mesh alumina grit as the base particles. The coatings on these particles exhibited extensive delamination, which was associated with the sharp contours of the angular particles. Replacement of the alumina grit with spheroidal particles resulted in a substantial improvement in coating quality. Other materials which have been coated are uranium, thorium, and boron carbides; europia; a gadolinia-samarium mixture; and thoria particles produced by a sol-gel process. There was no apparent influence of base-particle composition on appearance or properties of pyrolytic-carbon coatings for the deposition conditions investigated (1800°C maximum for uranium carbide and 1400°C maximum for other materials). Particle geometry, however, was significant in that the resistance of a coating of a given thickness to a compressive load was much greater for a higher degree of base-particle sphericity.

Descriptions and results of sixteen selected coating experiments are summarized in Table I. The process variables considered were (1) system pressure (150 to 762 mm Hg); (2) hydrocarbon species (CH_4 or C_2H_2) and partial pressure (20 to 500 mm Hg); (3) carrier-gas species (He or H_2); and (4) hydrocarbon flow rate (7 to 200 $\text{cm}^3/\text{min/g}$ of initial particle charge) and temperature (1000 to 1800°C). The results suggest

TABLE I
CONDITIONS AND RESULTS OF SELECTED EXPERIMENTS ON APPLICATION OF PYROLYTIC-
CARBON COATINGS TO SPHEROIDAL PARTICLES IN A FLUIDIZED BED

Run No.	Base Particles	Coating Temperature (°C)	Total System Pressure (mm Hg)	Hydrocarbon		Average Deposition Rate (μ/hr)	Average Coating Thickness ^a (μ)	Average Crushing Load per Particle ^b (g)	Microstructure
				Partial Pressure (mm Hg)	Flow Rate (cm ³ /min/g)				
45	UC ₂	1400	300	300(CH ₄)	40	118	45	609	laminar
37	UC ₂	1400	300	300(CH ₄)	40	48	85	1540	laminar
42	UC ₂	1400	300	300(CH ₄)	20	27	120	2339	laminar
41	UC ₂	1400	300	300(CH ₄)	40	38	170	3713	laminar
63	UC ₂	1400	300	300(CH ₄)	67	43	260	6865	laminar
67	ThO ₂ ^c	1400	250 ^d	250(CH ₄)	40	43	130	3009	laminar
69	ThO ₂ ^c	1400	250 ^d	50(CH ₄)	10	13	100	2412	columnar
82	ThO ₂ ^c	1400	762 ^d	254(CH ₄)	40	52	105	2657	laminar
83	ThO ₂ ^c	1400	762 ^e	254(CH ₄)	40	21	42	1775	laminar
32	Eu ₂ O ₃	1400	300 ^d	30(CH ₄)	7	8	65	f	columnar
36	Gd ₂ O ₃ -Sm ₂ O ₃	1400	300	300(CH ₄)	40	33	100	f	laminar
72	B ₄ C	1400	300	300(CH ₄)	200	57	114	2533	laminar
78	ThO ₂ ^c	1000	500	500(C ₂ H ₂)	60	117	117	4078	random, porous
79	ThO ₂ ^c	1100	500	500(C ₂ H ₂)	30	107	107	4357	random, porous
46	UC ₂	1800	150 ^d	20(CH ₄)	10	18	100	979	columnar
50	UC ₂	1800	200 ^d	40(CH ₄)	10	14	85	856	columnar

^aMeasured by random scanning of microradiograph.

^bMean value of 10 particles.

^cParticles made by sol-gel process.

^dHelium used as carrier gas.

^eHydrogen used as carrier gas.

^fNot measured.

that rates of coating application less than $18 \mu/\text{hr}$ yield predominantly columnar structures, while higher rates yield laminar structures.

Coated-particle crushing strength was found to depend directly on coating thickness, as illustrated in Table I by data from runs 45, 37, 42, 41, and 63. The crushing strengths of particles from runs 46 and 50, made at 1800°C , are somewhat lower than values obtained for the 1400°C coatings, but sufficient data are not available to draw conclusions about this point.

The large difference in average linear deposition rates observed between runs 45 and 37 and the smaller difference between rates of other runs where coating time was the only variable can be attributed to the fact that the instantaneous rate decreases as the coating thickness increases. A run is started with small uncoated particles, and as it progresses the particle surface area to be coated continuously increases. This results in a progressively slower linear carbon build-up if the supply of hydrocarbon gas is not increased during the run.

Data from runs 67, 69, 82, and 83 indicate that there is not a great difference in the deposition rates obtained by using added helium as a fluidizing agent with fixed flow rate and hydrocarbon partial pressure. However, the $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ reaction at the particle surfaces was apparently greatly retarded by substituting hydrogen for helium. Figure 5 shows the product of run 69, in which a columnar coating was applied to sol-gel ThO_2 .

The densities of coatings produced at 1800°C in runs 46 and 48 were 2.08 and 2.10 g/cm^3 , respectively, compared with a density range of 1.43 to 1.92 g/cm^3 for coatings deposited at 1400°C . Density has

Fig. 5. Sample of Pyrolytic-Carbon Coated Sol-Gel ThO_2 from Run 69. Coating applied at 1400°C . Polarized light. 100X.

not been measured on coatings deposited below 1400°C. The above values were obtained by cracking the coated particles to separate the coatings from the cores, leaching the fragmented coatings to assure removal of all heavy metal, and determining the density on the clean coatings by means of a helium pycnometer.

The coatings produced at 1000 and 1100°C in runs 78 and 79 from acetylene were intended to be porous, but the crushing strengths indicate that they are not sooty buildups.

Fueled Graphite Fabrication Studies
(A. J. Taylor and J. M. Robbins,
Metals and Ceramics Division)

The amount of damage sustained by pyrolytic-carbon coated carbide fuel particles during fabrication in a graphite matrix was determined. The principal objective of the work was to determine the maximum concentration of coated particles that could be incorporated in a graphite matrix under various cold-forming pressures without causing more than some minimum amount of damage to the particle coatings. Fuel loadings ranged from approximately 6 to 23 vol % of coated particles and forming pressures ranged from 3,000 to 35,000 psi. The baked specimens were electrolyzed in acid and the coating damage was assessed by the uranium concentration in the leach solution.

Materials

The coated particles tested were from Lot 3M-117 and consisted of natural uranium carbide spheroids with an average diameter of 176 μ coated with a laminar layer averaging 98 μ in thickness. Both the apparent density, as measured with helium, and the bulk density, as

measured by a plastic-embedment technique, were 2.5 g/cm^3 . The coated particles contained 44.10 wt % U, and 4.62×10^{-4} wt % of the contained uranium in the as-received material was leachable.

The filler used in the matrix was a blend of 50 wt % natural graphite having an average particle size of 10μ and 50 wt % synthetic graphite having an average particle size of 2μ . The binder was a furan resin designated as Varcum No. 8251.

Experimental Procedure

Body preparation consisted of blending the coated particles, graphite filler, and furan resin in benzene. After gentle mixing until a slightly damp state was reached, the material was passed through an 18-mesh screen. The resulting granules were dried overnight at 45°C to remove the remainder of the benzene.

The specimens were formed initially by placing a weighed charge in a cylindrical die and lightly pressing at 100 psi. The pellets were then enclosed in a rubber sheath, evacuated, and warm molded isostatically in an autoclave containing water at 100°C and 1200 psi. Next, the sheathed pellets were isostatically pressed in oil at room temperature to pressures of 3,000, 6,000, 9,000, 12,000, 15,000, 20,000, 25,000, and 35,000 psi. (For the body with the highest fuel concentration, the maximum pressure used was 12,000 psi.) All specimens were baked on a 24-hr schedule to 1000°C in a hydrogen atmosphere.

Anodic disintegration of the specimens was accomplished with a 3-v, 2-amp dc circuit in 8 M HNO_3 . The disintegration required from 16 to 24 hr, depending on forming pressure and/or bulk density of the specimen. After filtering and rinsing, the residue was leached for 24 hr at 95°C in an 8 M HNO_3 solution and the solution analyzed for uranium.

Results

The results of the experiments are given in Table II. It is seen that, as one would expect, the coating damage increases with forming pressure and fuel loading. The data indicate that, if fission-product retention requires, for example, the fraction of coatings damaged to be limited to the order of 10^{-4} , then the forming pressures for 7 vol % loadings would be limited to about 12,000 psi. Forming pressures of 12,000 and 9,000 psi would be suitable, in this case, for loadings of 13 and 16 vol %, respectively, and 6,000 psi could be used for loadings as high as 21 vol %.

EVALUATION AND IRRADIATION TESTING

The evaluation and irradiation testing program has been concerned primarily with vendor-supplied coated-particle materials. Materials have been supplied by the Minnesota Mining and Manufacturing Company (3M), National Carbon Company (NCC), High Temperature Materials, Incorporated (HTM), General Atomic (GA), Nuclear Materials and Equipment Company (NUMEC), and Speer Carbon Company (SCC).

This portion of the program is conveniently divided into two sections, tests on unsupported pyrolytic-carbon coated carbide particles and tests on graphite matrix elements containing coated particles.

Unsupported Coated Particles
(F. L. Carlsen, Jr., and J. L. Scott,
Metals and Ceramics Division)

Preirradiation Evaluation (E. S. Bomar, J. L. Cook, and R. J. Gray,
Metals and Ceramics Division)

Evaluation of coated particles has been directed toward the establishment of relationships between properties that are measurable

TABLE II
EFFECT OF FORMING PRESSURE AND FUEL LOADING ON
DAMAGE TO PYROLYTIC-CARBON COATED PARTICLES
DURING FABRICATION IN GRAPHITE MATRICES

Forming Pressure (psi)	Coated Particle Concentration (vol %)	Coated Particles Damaged ^a (%)
3000	5.8	0.01
	10.5	0.005
	14.8	0.01
	18.8	0.04
6000	6.3	0.01
	11.7	0.02
	15.7	0.025
	20.8	0.01
9000	6.9	0.01
	12.0	0.01
	16.4	0.015
	22.3	0.14
12,000	7.0	0.02
	12.7	0.02
	17.7	0.45
	23.1	0.15
15,000	7.4	0.06
	13.0	0.13
	18.5	0.225
20,000	7.8	0.14
	13.5	0.06
	19.2	0.33
25,000	7.8	0.06
	13.6	0.18
	19.7	0.58
35,000	8.1	0.06
	13.8	0.50
	19.8	1.28

^aBased on uranium content of acid electrolysis solution.

prior to irradiation and behavior during irradiation. Evaluation includes determination of structure, shape, and dimensions of the core particles and their coatings; amount of the exposed fuel; impurity content; density; crushing strength; and effect of heat treatments. Descriptions of the majority of these measurements were given previously in some detail (4).

Table III presents results of examining coated particles used in experiments, discussed in this section and the following section, with both unsupported particles and fueled graphite bodies. Figure 6 is a typical photomicrograph of a triplex pyrolytic-carbon coated uranium carbide particle. A duplex pyrolytic-carbon coating structure on uranium-thorium carbide is shown in Fig. 7.

A technique has been developed for studying the nature of crack propagation in pyrolytic-carbon coating. The origin of the study lies in the observation that the cracks that initiate at the coating-particle interface of irradiated coated particles seem to stop at the interface between the laminar and columnar layers of NCC duplex coatings (5). Individual coated particles are cracked between the anvils of a micrometer. The coated particle is placed upon the adhesive side of Scotch tape and then the micrometer is slowly advanced until the coating cracks. Cracking is observed with the aid of a microscope. After unloading of the micrometer, separation of the fragments allows examination of the fracture surfaces. The Scotch tape is useful as a manipulating aid and in retaining the position of the fragments of the coating.

TABLE III
RESULTS OF EVALUATION OF FULLY ENRICHED FUEL PARTICLES

	GA-308	GA-309	GA-310	NCC-207	NCC-208	NCC-209	NCC-215	SCC-500
Core Material	UC ₂	UC ₂	(U,Th)C ₂	UC ₂	(U,Th)C ₂	UC ₂	UC ₂	(U,Th)C ₂
Uranium Content (wt %)	29.6	35.7	14.4	44.30	19.57	43.18	40.4	24.5
Thorium Content (wt %)			9.0		13.44			14.9
Particle Dimensions (μ)								
Total particle, av	537	377	470	422	445	402	388	381
Core particle, av	230	182	175	220	213	223	219	179
Coating thickness, av	154	97	148	101	117	90	85	101
Coating Structure	triplex	triplex	triplex	columnar	duplex	duplex	duplex	laminar
Pour Density (g/cm ³)	1.7	1.7	1.5	2.0	1.6	2.0	1.9	1.5
Particle Weight, av (g × 10 ⁻⁴)	2.0	0.8	1.4	1.1	1.2	1.2	1.0	0.7
Coated Particle Density ^b (g/cm ³)	2.61	2.76	2.37	3.30	2.79	3.36	3.22	2.31
Surface Area (m ² /g × 10 ⁻³)	24.0	53.0	52.0	26.0	c	c	17.0	170
Crushing Load, av (g)	1785	964	1598	1240	1473	1022	1179	1290
Surface Contamination (% U × 10 ⁻³)	5.4	3.8	2.4	2.3	1.8	4.9	2.2	0.2
Fuel Removal (% U × 10 ⁻³)	2.8	0.2	0.2	< 0.1	< 0.5	< 0.2	1.0	0.2

^aSCC-500 identifies material prepared by the 3M Company and sold to Speer Carbon Company for use in fabrication of fueled spheres.

^bMeasured with helium pycnometer.

^cNot measured.

Fig. 6. Typical Triplic Pyrolytic-Carbon Coated Uranium Carbide Particles from Batch GA-308. 100X. Bright field.

Fig. 7. Typical Duplex Pyrolytic-Carbon Coated $(Th,U)C_2$ Particles from Batch NCC-208. 150X. Bright field.

Duplex NCC and triplex GA coatings have been observed to crack through the outer layer, which separates from the rest of the coated particle as shown in Fig. 8. This indicates that there is little or no bonding between the two layers. Single-layer and multilayer coatings with good bonding (i.e., PyC-SiC-PyC or duplex coatings prepared by decreasing deposition rates at 1400°C) fracture completely through the coating to the carbide particle, as shown in Fig. 9.

It is anticipated that this technique will be useful in determining if the nature of the interface between multilayer coatings is an important parameter for irradiation performance.

Irradiation Tests (P. E. Reagan and R. M. Carroll, Reactor Chemistry Division; E. L. Long, Metals and Ceramics Division)

Capsule B9-11 containing duplex pyrolytic-carbon coated uranium-thorium carbide particles (Batch NCC-208-2) was irradiated in the B9 sweep facility. The particles were irradiated in a flux of 1.2×10^{14} neutrons/cm²·sec at 2050°F to 14.7% heavy metal burnup. During irradiation, the duplex particles released fission gas at a lower fractional release rate than any other particles irradiated in the current series of experiments. The average fission-gas release rates, expressed as the ratio of release rate to birth rate (R/B), are listed in Table IV. No broken particles were detected visually or metallographically during postirradiation examination. The only observable change was at the core-coating interface where wedge-shaped fractures developed, as shown in Fig. 10.

Capsule B9-12 was prepared using coated particles from the same batch as B9-11. This capsule was first irradiated for 4 days at 2150°F

Fig. 8. Cracked Pyrolytic-Carbon Coating, Batch GA-308. Note the lack of bonding between layers of coating.

Fig. 9. Cracked PyC-SiC-PyC Coating, Batch GA-306, with Fracture Through the Layer Interfaces.

TABLE IV
SUMMARY OF OPERATING AND FISSION-GAS RELEASE
DATA FOR ORR B9 AND C1 SWEEP CAPSULES

Capsule No.	Particle Batch No.	Irradiation Temperature (°F)	Burnup (at. %) ^a	Average Ratio of Release Rate to Birth Rate (ppm)				
				Kr ^{85m} ^b	Kr ⁸⁷	Kr ⁸⁸	Xe ¹³³	Xe ¹³⁵
B9-11	NCC-208-2	2050	14.7	1.23	0.66	0.94	1.80	0.41
B9-12	NCC-208-2	2150-2300	2.4	3000	1200	1300	2800	3800
B9-13	GA-308	2300-2400	8.0	28	22	25	24	15
B9-14	GA-309	2500	20	36	28	32	19	7
C1-11	GA-310	2050	4.5	4.5	2.8	3.6	2.3	1.2

^aHeavy metal burnup.

^bValues for Kr^{85m} are based on a yield of 2%.

Fig. 10. As-Polished Microstructure of Typical $(U,Th)C_2$ Coated Particles from Batch NCC-208-2 After Irradiation in Capsule B9-11. 100X.

and then for about 20 hr at 2300°F. After 11 hr at 2300°F, instruments monitoring the helium sweep line began detecting numerous activity bursts. About fifty bursts were detected during the subsequent 9-hr period. After 20 hr at 2300°F, the temperature was reduced to 2150°F, but the fission-gas release continued to increase for the next two days. Then the test was terminated. By that time, it appeared that a large portion of the coatings must have broken. The capsule was irradiated to 2.4 at. % heavy metal burnup. The fission-gas release rates given in Table IV reflect the high rates during the last three days of the irradiation.

During postirradiation examination of capsule B9-12, several half shells with the cores missing were observed, and some bonding of the particles was evident. A metallographic examination disclosed no broken coatings, but a few wedge-shaped fractures at the core-coating interface were observed (similar to those shown for B9-11 in Fig. 10). These fractures penetrated less than one third of the inner coating thickness, and there was no clear evidence of reaction zones.

Capsule B9-13 was prepared using triplex pyrolytic-carbon coated uranium carbide particles from batch GA-308. This capsule was irradiated to 8 at. % burnup at 2300 to 2400°F. The average fission-gas release rates for most of the irradiation period are listed in Table IV. Toward the end of irradiation, the specimen temperature was increased from 2300 to 2400°F. A burst of activity was detected in the helium sweep line. The temperature was reduced to 2300°F and the activity level decreased. Three days later the temperature was again increased to 2400°F. A slight heating burst was observed. After 130 min at 2400°F,

several activity bursts were detected, and during the following 8 hr at 2400°F numerous additional bursts occurred, increasing the gross gamma activity of the sweep gas by 100 to 1000 times. The experiment was withdrawn after this period because the sweep-gas activity reached the safety limit.

No broken particles were detected visually or metallographically during postirradiation examination, but numerous cracked uranium carbide cores such as shown in Fig. 11 were observed. However, the core cracks did not extend into the coating, and there were no reaction zones at the core-coating interface. An 8-hr acid leach of a 0.010-g sample of particles in 8 M HNO_3 yielded 0.11 mg U, 3.7% of the uranium contained in the sample. It might be concluded that either 3.7% of the particle coatings failed, that 3.7% of the uranium diffused through the coatings, or that some combination of these two possibilities occurred. Another possibility is that a number of coated particles fragmented and the pieces adhered to the capsule walls or other locations where they remained unobserved. This appears to be substantiated by post-irradiation microradiography, which indicated heavy metal, presumably uranium, on the surface of one of four particles examined but showed none in the coatings.

Capsule B9-14 was prepared using triplex pyrolytic-carbon coated uranium carbide particles from batch GA-309. This capsule was irradiated to about 20 at. % U at 2500°F, with the exception of a 46-hr period at 2400°F after a burnup of 10 at. % U had been attained. This burnup corresponds to an integrated fast flux of about 3.3×10^{20} nvt ($E > 0.18$ Mev). The average fission-gas release rates are listed in Table IV. No activity bursts occurred during this experiment.

Fig. 11. As-Polished Microstructure of Typical Coated Uranium Carbide Particles from Batch GA-308 After Irradiation in Capsule B9-13. 100X.

Capsule Cl-11 was prepared using triplex type pyrolytic carbon-coated uranium-thorium carbide particles from batch GA-310. This capsule is now in the reactor and has been irradiated at 2050°F to 4.5 at. % heavy metal burnup. The average fission-gas release rates are listed in Table IV. No activity bursts have been observed to date.

Summary and Discussion

On the basis of capsule B9-14 results, it is concluded that uranium carbide particles with triplex pyrolytic-carbon coatings exhibit excellent noble-gas retention properties to heavy metal burnups of 20% when irradiated at a constant temperature of up to 2500°F. In the previous irradiation test on similar unsupported coated particles (B9-13), some escape of fission gas was encountered when relatively small temperature changes were experienced by the coated particles. At the present time, this behavior is not understood. The difference in behavior may be the result of either differences in the individual batches of particles or the effects of thermal cycling. Further tests are scheduled to clear up the present uncertainties.

Fueled Graphite Spheres
(F. L. Carlsen, Jr., and J. L. Scott,
Metals and Ceramics Division)

Preirradiation Evaluation (E. S. Bomar, F. L. Carlsen, Jr., and J. L. Cook,
Metals and Ceramics Division)

During the past year, 60 fueled graphite spheres, either 1 1/2 in. or 6 cm in diameter, have been irradiated. The variations under study include manufacturer, unfueled shell thickness, and process for fabricating the unfueled shells. Six manufacturers have supplied fueled graphite spheres with unfueled shell thicknesses ranging from 1/16 to 0.43 in. and

many spheres without shells. The fueled cores were prepared by mixing coated particles with graphite flour and binder, molding by cold, warm, or hot pressing, and then baking at 1400 to 1900°C. The unfueled shells were formed either by molding with the fueled core or by machining from graphite stock. The fuel cores were placed in the machined shells, the mating surfaces were bonded with carbon cement, and the assembled spheres were baked at 1000°C to carbonize the cement.

The preirradiation evaluation of the spheres included visual and dimensional inspections, density determinations, determinations of the distribution of coated particles, measurements of exposed fuel and fuel loading, metallographic examinations, and strength measurements. Some of the characteristics of the spheres used in the irradiation experiments are given in Table V. The methods and procedures used for the preirradiation evaluation have been fully reported elsewhere (6, 7, 8, 9).

The spheres were received in lots of 4 to 10 along with control spheres, which contained natural uranium. The spheres for the irradiation capsules were selected on the basis of the results of the pre-irradiation evaluation.

Irradiation Tests (V. A. DeCarlo, F. R. McQuilkin, and C. L. Segaser, Reactor Division; J. L. Scott and C. Michelson, Metals and Ceramics Division)

Sweep Capsule Tests. Fueled graphite spheres containing coated particles have been irradiated in flowing helium in the ORR-Poolside sweep-gas facilities. Two capsule designs have been used and are shown in Fig. 12. The "4-Ball" capsules are used for 1 1/2-in.-diam spheres, while the "AVR" capsules are used for 6-cm-diam spheres. There are two compartments in each capsule, one that is swept continuously

TABLE V
CHARACTERISTICS OF FUELED GRAPHITE SPHERES IN IRRADIATION EXPERIMENTS

Lot No.	Fabrication Process	Unfueled Shell Thickness (in.)	Coated Particle Batch No.	Heavy Metal Content (g/Sphere)	Coated Particle Content ^a (vol %)	Bulk Density (g/cm ³)	Crushing Strength ^g (lb)	Exposed Uranium (%)	Irradiation Capsule Designation
1 1/2-in. Diameter								$\times 10^{-2}$	
GA-S1	Molded	None	GA-302	3.16	6.6	1.87	1475 ^f	50	06Z-6
GA-S8	Molded ^b	1/4	GA-302	3.16	22.1	1.90	1170 ^f	103	08A-6
GA-S9	Molded ^b	1/4	GA-302	3.16	22.1	1.93	1120 ^f	e	08A-6
GA-S10	Molded ^b	None	GA-302	3.16	6.6	1.87	1430 ^f	e	05X-6
3M-S4	Molded	None	3M-120	3.16	13.1	1.78	3060	0.6	05Z-6
3M-S5	Molded	1/16	3M-120	3.16	17.0	1.79	3240	1.8	06X-6
NCF-S2	Molded	None	NCC-208	3.16	12.4	1.78	1640	9.0	05X-6, 06X-6, 06Z-6
NCF-S4	Molded	None	NCC-209	5.0	13.5	1.82	1290 ^f	e	Loop 2-1
NCF-S5	Molded	None	NCC-208	2.54	7.9	1.82	1100 ^f	e	F1-8B-1
NCF-S6	Molded	1/4	NCC-208	2.54	26.5	1.78	760	e	F1-8B-1; -2
			NCC-211						
NCF-S7	Molded	1/4	NCC-208	3.6	42.5	1.80	e	5.0	06X-6
NCF-S9	Molded	None	NCC-208	2.54	7.9	1.69	e	e	F1-8B-2
			NCC-211						
NCP-SS1	Machined (ZTA) ^c	0.43	NCC-207	0.60	16	1.87	1225	0.2	08-6
NU-SS3	Machined ^b (ALSw/AMT)	0.52		0.63	None	1.87	e		F1-8B-2
ORNL-SS1	Machined (R-0020)	0.43	NCC-BE 3M-115	2.41	60	1.88	e	e	08-6

TABLE V (continued)

Lot No.	Fabrication Process	Unfueled Shell Thickness (in.)	Coated Particle Batch No.	Heavy Metal Content (g/Sphere)	Coated Particle Content ^a (vol %)	Bulk Density (g/cm ³)	Crushing Strength ^g (lb)	Exposed Uranium (%)	Irradiation Capsule Designation
								$\times 10^{-2}$	
<u>1 1/2-in. Diameter</u>									
SCC-S15	Molded	1/8	SCC-500	2.54	15.9	1.79	1190	2.0 ^f	F1-8B-2
SCC-S16	Machined ^d	0.20	SCC-501 SCC-500 SCC-501	2.54	31.0	1.77	e	2.0 ^f	F1-8B-3
<u>6-cm Diameter</u>									
GA-VS11	Machined (ATJ)	0.43	GA-310	10	47.0	1.75	e	e	05-7
GA-VS12	Molded	1/4	GA-310	10	24.0	1.85	e	e	01-7; 08-7
3M-VS14	Molded	None	3M-120	10	10.7	1.76	e	e	01-7
NCF-VS14	Machined (AGOT)	0.40	NCC-211 NCC-215	10	e	1.83	e	e	01-7
NCF-VS15	Machined (ATJ)	0.40	NCC-211 NCC-215	10	e	1.73	e	e	05-7

^aVolumetric loading in fueled region.^bImpregnated to reduce permeability.^cGraphite grade used for unfueled shell.^dUnfueled shells made from grades ATJ, AGOT, C-18, and CS-312.^eNot determined.^fDetermined from similar spheres.^gLoad required to cause fracture of fueled spheres.

Fig. 12. Irradiation Capsules for Fueled Graphite Spheres.

with helium and a second that is static. Two spheres are contained in the sweep-gas compartments of the "4-Ball" capsules, while only one sphere is in the sweep-gas compartments of the "AVR" capsules. The helium sweep gas is continuously monitored for gross gamma activity and periodically analyzed for the noble fission gases $\text{Kr}^{85\text{m}}$, Kr^{87} , Kr^{88} , Kr^{91} , Xe^{133} , Xe^{135} , Xe^{140} , and Xe^{141} .

Spheres in the "4-Ball" capsules were irradiated at surface temperatures of 600 to 1500°F and power densities of 16 to 65 w/cm³ of fueled sphere, resulting in center temperatures of approximately 900 to 1800°F. The spheres in AVR capsules were irradiated at surface temperatures of 1550 to 2000°F, power densities of approximately 18.5 w/cm³, and corresponding center temperatures of 2400 to 2600°F. A summary of the results of sweep-gas experiments is given in Table VI. Fueled graphite spheres are also being tested in the ORR Loop-2 facility, but results are not presently available in terms of fractional fission-gas release.

Static Capsule Tests. Spheres are irradiated in static helium in the "8-Ball" capsules and in the static compartments of the "4-Ball" and "AVR" capsules shown in Fig. 12. The irradiation conditions were similar to those for the sweep-gas capsules and are summarized for the "8-Ball" capsules in Table VII. The F1-8B-1 and F1-8B-2 capsules were irradiated for 7 weeks (one ORR cycle) while the F1-8B-3 capsule will be irradiated for two cycles.

Postirradiation Examinations (J. G. Morgan, M. F. Osborne, and D. R. Cuneo, Reactor Chemistry Division)

The postirradiation examination of eight capsules, containing forty 1 1/2-in.-diam spheres, has been partially completed. All 38 spheres,

TABLE VI
SUMMARY OF RESULTS OF SWEEP-GAS EXPERIMENTS
ON FUELED GRAPHITE SPHERES

Capsule No.	Sphere Designation	Unfueled Shell		Surface Temperature (°F)	Power Density (w/cm ³)	Burnup (at. % HM ^a)	Kr ⁸⁸ (R/B) ^e
		Thickness (in.)	Process				
1 1/2 in. Diameter							
06Z-6	NCF-S2	None		1450	45	5.2	$< 10^{-10}$
08-6	NCP-SS1	0.4	Machined	1050	16	11.1	4×10^{-5}
05Z-6	NCF-S2M ^b	None		1450	45	3.6	1.5×10^{-5}
06X-6	NCF-S7	1/4	Molded	1500	65	3.5	1×10^{-5}
08A-6	NCF-S7	1/4	Molded	1500	45	4.4	2×10^{-5}
6-cm Diameter							
01-7 ^c	GA-VS-12	1/4	Molded	1720 ^d	18.5	~ 0.8	3×10^{-4}
05-7 ^c	GA-VS-11	0.43	Machined	1730 ^d	18.5	~ 0.8	1.5×10^{-3}
08-7 ^c	GA-VS-12	1/4	Molded	1750 ^d	18.5	~ 0.8	2×10^{-4}

^aBurnup values based on total amount of heavy metal (HM).

^bSame as NCF-S2 except that the surface of the spheres were machined and chlorine treated to remove exposed fuel.

^cIrradiation in progress.

^dCentral temperatures of approximately 2450°F.

^eRatio of release rate to birth rate.

TABLE VII
SUMMARY OF OPERATING CONDITIONS FOR
8-BALL IRRADIATION CAPSULES

Capsule Number	Sphere Number	Position	Central Temperature (°F)	Surface Temperature (°F)	Power Density (w/cm ³)	Burnup (at. % HM ^a)
F1-8B-1	NCF-S5-4	1 (top)	1250	1040	36	10.4
	NCF-S6-1	2		1207	38	11.0
	NCF-S5-5	3		1217	39	11.3
	NCF-S6-3	4		1238	40	11.5
	NCF-S5-10	5		1259	41	11.8
	NCF-S6-9	6				
	NCF-S5-11	7		1165	37	10.7
	NCF-S6-11	8 (bottom)		1053	33	9.5
F1-8B-2	NCF-S6-10	1 (top)	1440	1090	38	11.0
	SCC-S15-3	2		1145	40	11.5
	NCF-S9-3	3		1145	40	11.5
	NU-SS3-1	4		1070	27	6.2
	NU-SS3-2	5		1085	28	6.2
	NCF-S9-6	6		1120	39	11.3
	SCC-S15-5	7		1090	38	11.0
	NCF-S9-4	8 (bottom)		1030	35	10.1
F1-8B-3 ^b	SCC-S16-5	1 (top)	1372	1090	38	11.0
	SCC-S16-7	2		1150	40	11.5
	SCC-S16-3	3		1130	40	11.5
	SCC-S16-1	4		1145	40	11.5
	SCC-S16-6	5		1170	41	11.8
	SCC-S16-10	6		1180	41	11.8
	SCC-S16-4	7		1025	39	11.3
	SCC-S16-2	8 (bottom)		1090	38	11.0

^aEstimated burnup values based upon heavy metal content of coated particles containing 93% enriched uranium.

^bIrradiation in progress.

which contained coated particles, were found to be sound and without cracks or other gross changes. Only very small dimensional and weight changes occurred. The spheres showed changes of 0 to ± 4 mils in the pole diameters (parallel to the molding direction), while a few of the spheres shrank by 10 to 22 mils in the equatorial diameters (perpendicular to the molding direction). The spheres generally lost about 10 mg (0.02%), but weight losses of 150 mg (0.3%) were observed for the two spheres irradiated in the sweep section of the 06Z-6 pool-side capsule. The crushing strengths of several irradiated spheres, given in Table VIII along with the dimensional changes, indicate that irradiation has caused no significant loss of strength.

The two NU-SS-3 spheres irradiated in the F1-8B-2 capsule were the only spheres that failed under irradiation. These elements did not contain coated particles, but each contained a cylindrical insert made by mixing U_3O_8 with natural graphite, pressing without a binder, and baking in vacuo at $1900^\circ C$ to convert the oxide to dicarbide. The insert was placed in a machined graphite, grade ALSw/AMT, shell and given four impregnations. Visual inspection revealed that the caps on both of these spheres popped out due to the irradiation-induced growth of approximately 30% by the inserts. One of these spheres is shown in Fig. 13.

Summary and Discussion

Fueled graphite spheres made by six manufacturers, with and without unfueled shells and having a very wide range of properties, have been irradiated. The fission-gas release rates have generally been acceptable, although higher than for unsupported coated particles. The

TABLE VIII
RESULTS OF POSTIRRADIATION EXAMINATION
OF FUELED GRAPHITE SPHERES

Capsule No.	Sphere Design- nation	Unfueled Shell		Average Diameter Change (%)		Precrushing Strength (lb)	Postcrushing Strength (lb)
		Thickness (in.)	Process	Pole	Equator		
06Z-6	NCF-S2	None		+0.01	-1.13	1640(3) ^a	1425(3) ^a
Loop 2-1	NCF-S4	None		+0.12	-0.58	1290(3)	1430(3)
8B-1	NCF-S6	1/4	Molded	+0.12	-0.01	760(2)	690(3)
08A-6	GA-S8	1/4	Molded	+0.08	+0.51	1170(3)	975(1)
	GA-S9	1/4	Molded	+0.02	+0.11	1120(3)	1075(1)
08-6	NCF-SS1	0.43	Machined	+0.11	+0.05	1225(3)	1325(2)

^aNumbers in parentheses indicate number of spheres tested.

Fig. 13. Sphere No. NU-SS3-2 After Irradiation in Capsule F1-8B-2.
1 1/2X.

higher release is thought to be due to some fracturing of coated particles during fabrication. None of the fuel elements containing coated particles, including those with molded unfueled shells, have cracked or shown other evidences of irradiation-induced mechanical failure. Only small dimensional and weight changes have occurred and no significant loss of strength has been experienced.

These experiments have shown that fueled graphite spheres containing coated particles have a considerable potential for nonpurged gas-cooled reactors.

SUPPORTING RESEARCH

Compatibility of Fueled Graphite Spheres with Water Vapor
(J. P. Blakely, J. L. Rutherford, and L. G. Overholser,
Reactor Chemistry Division)

The results of experimental studies of the compatibility of unsupported pyrolytic-carbon coated particles with water vapor were reported earlier.⁽¹⁰⁾ These studies indicated that some lots of the unsupported particles had coatings that were protective when contacted with steam at temperatures of 900 to 1000°C for several hours, whereas the coatings on other lots of particles failed to a marked degree under similar conditions. The compatibility of various fueled graphite spheres with water vapor has also been studied in the temperature range of 800 to 1000°C. The rate of reaction of the fuel body with steam, the incidence of failure of the body, and the rate of production of hydrogen have been determined for a number of lots of fueled graphite spheres. The rate of hydrogen formation is of interest in the assessment of hazards arising from inleakage of water and subsequent attack of the

hot fueled graphite spheres. The reaction of steam with unfueled graphite spheres has also been studied, mainly to provide some basis for comparison between well-graphitized material and the carbon present in the fueled spheres.

Measurements were made at 800, 900, and 1000°C using 1.5-in.-diam fueled and unfueled graphite spheres. A partial pressure of water vapor of approximately 730 mm (Hg) was employed at a flow rate of approximately 600 cm³/min. The exit steam was condensed and the reaction products were dried prior to venting through a manifold equipped for gas sampling. The reaction rates reported are averages based on weight changes obtained from weighings made before and after exposure to steam over a 4- to 5-hr period. The effluent gases were analyzed by the Analytical Service Groups using a gas chromatograph and, in a few cases, a mass spectrometer. The analytical results were used to establish the rate of hydrogen production as well as for the calculation of reaction rates of the graphite body.

Reaction rates obtained for spherical specimens of Speer Mod-2 and ATJ grades of graphite at different degrees of burnoff are plotted as a function of temperature in Fig. 14. The striking feature of these results is the increase in reaction rates with the degree of burnoff of the specimens. It was anticipated that some effect would be observed at low burnoffs but, at least in the case of the ATJ graphite, the rates increased after a 5 to 10% burnoff. This behavior makes it more difficult to compare reaction rates of different materials and to determine the effect of variables such as the temperature and partial pressure of steam on the reaction rate. The ATJ grade appears to be

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Fig. 14. Arrhenius Plots of the Steam Reaction with Speer Mod-2 and ATJ Graphites.

about twice as reactive as the Speer Mod-2 grade. The latter has a lower ash content, which may be responsible for the lower reactivity. The reasonably linear plots obtained at the higher burnoffs correspond to an activation energy of approximately 60 kcal/mole. The fact that the reaction rates were not constant, but increased with burnoff, introduces some uncertainty in the activation energy. An extreme case of this behavior is shown by the Speer Mod-2 specimen at low burnoff. Here the activation energy increased with increasing temperature due to the burnoff effect. The curvature found in some of the other plots is also due to this effect.

Reaction rates obtained for various lots of fueled graphite spheres are plotted as a function of temperature in Fig. 15. Values for the SCC spheres are given only at 900°C because of early failure at 1000°C and abnormally large weight losses at 800°C - the latter due to excessive outgassing. The maximum variation in reaction rates for the various lots of fueled spheres is about fivefold if lot GA-S5 is excluded. This lot was impregnated and therefore not strictly comparable to the other lots. Comparison of these rates with those given in Fig. 14 indicates that the reactivity of the fueled spheres is not very different from that found for Speer Mod-2 and ATJ grades of graphite. The slope of the plots in Fig. 15 corresponds to an activation energy of approximately 60 kcal/mole, which is about the same as that found for the unfueled graphites. As noted previously, the change in reactivity with burnoff introduces some uncertainty in the comparisons.

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Fig. 15. Arrhenius Plots of the Steam Reaction with Various Fueled Graphite Spheres.

Reaction rates obtained at 900°C for most of the fueled spheres examined are listed in Table IX. Hydrogen production rates and CO/CO₂ ratios obtained from analyses of the effluent gases also are included. The data indicate that the presence of unfueled shells had no significant effect on the reaction rates. The one impregnated lot (GA-S5), on the other hand, reacted substantially slower. All of the lots of SCC spheres were more reactive than any of the other lots examined, and those that were exposed to steam for 1 hr at 1000°C failed. These failures at 1000°C are due only in part to the higher reaction rates. Fueled spheres from the GA and 3M lots remained intact at comparable or higher burnoffs. This suggests that the attack of the SCC spheres was concentrated on the residual binder material. Some of the SCC spheres failed at burnoffs as low as 4%. Examination of the coated particles after failure of the spheres showed no significant attack of the pyrolytic-carbon coatings.

The CO/CO₂ ratios found in the effluent gases varied considerably. The SCC spheres gave ratios of 5 to 6 compared to ratios of less than 1 for some of the other spheres. The cause of this variation is not known. If the primary reaction products are assumed to be H₂ and CO, then the production of CO₂ by the reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ would have occurred at different rates to yield the range of CO/CO₂ ratios observed. On the other hand, the variation may have been caused by the appearance of CO₂ as a primary reaction product. A larger CO/CO₂ ratio was found in the effluent gas from Speer Mod-2 graphite than from ATJ graphite. The CO/CO₂ ratio is of interest as a measure of the amount of hydrogen produced per unit of carbon reacted. Irrespective of the

TABLE IX
 REACTIVITY OF VARIOUS FUELED GRAPHITE SPHERES WITH STEAM AT 900°C
 (partial pressure of steam ~ 730 mm; flow rate ~ 600 cm³/min)

Sphere Designation	Unfueled Shell	Reaction Rate ^a (mg of C/g·hr)	Hydrogen Produced (cm ³ /g·hr)	CO/CO ₂ in Effluent Gas
NCF-S1-4D	None	1.7	5.9	2.9
NCF-S3-R1	None	1.3	4.7	2.4
3M-S2-23	None	2.9	12	0.5
3M-S3-15	1/16 in.	2.4	14	1.0
3M-S3-18	1/16 in.	2.4	12	1.0
3M-S6-18	1/8 in.	2.9	16	0.6
3M-S6-19	1/8 in.	2.5	14	0.7
SCC-S5-3	None	3.2	7.8	6.1
SCC-S5-7	None	4.1	12	5.5
SCC-S6-18	1/16 in.	3.4	8.5	5.7
SCC-S7-11	1/8 in.	4.8	13	5.7
SCC-S7-13	1/8 in.	3.5	9.7	5.6
SCC-S8-13	1/4 in.	4.2	11	4.5
SCC-S8-15	1/4 in.	4.7	13	5.3
GA-S3-6	None	1.5	7.5	0.4
GA-S3-11	None	1.2	7.5	0.1
GA-S3-14	None	1.2	7.7	0.3
GA-S4-9	1/4 in.	1.0	5.8	0.7
GA-S4-13	1/4 in.	0.87	4.1	0.4
GA-S5-11	None, Imp ^c	0.25	0.5	1.5
GA-S5-17	None, Imp ^c	0.28	0.7	2.8
GA-S5-18	None, Imp ^c	0.09 ^b	0.3	2.7

^aRates given are for burnoffs ranging from 0.5 to 1.5%.

^bThis sphere had been degassed at 1000°C prior to oxidation.
 The low rate is due at least in part to a burnoff of less than 0.05%.

^cImpregnated to reduce permeability.

mechanism, the volume of hydrogen formed per unit of carbon reacted will increase as the CO/CO_2 ratio decreases.

Diffusion of Heavy Metals in Pyrolytic and Porous Carbons
(R. B. Evans III and J. Truitt,
Reactor Chemistry Division)

An important phase of an experimental investigation of actinide migration in pyrolytic carbon is nearly complete. This work involves the determination of diffusion coefficients for thorium, protactinium, and uranium as a function of temperature by employment of the classical instantaneous-source-layer technique. The massive pyrolytic carbon under investigation possesses a columnar microstructure composed of highly oriented turbostratic crystallites which leads to the unusual anisotropic characteristics associated with materials of this type. Thus two sets of coefficients are required: one for diffusion perpendicular to the deposition plane (denoted as $D_{\perp}$), another for diffusion parallel to this plane (denoted as $D_{\parallel}$).

It would be most desirable to refer the coefficients to basal planes; however, the plane of deposition is used as a reference here, since the layers within the conical grains of the pyrolytic carbon are curved giving rise to "wrinkled sheets." These sheets are parallel to the deposition plane only on an average basis. Clearly the subject coefficients will not be as meaningful as the analogous coefficients for graphite crystals, since the latter would be principal components of a tensor referred to the "a" and "c" axes - while $D_{\perp}$ and $D_{\parallel}$ are merely phenomenological parameters. One should note also the non-equivalence of pyrolytic carbons as they occur in massive specimens and in fuel particle coatings. Regardless of these considerations, it

is anticipated that the present results will be of some value from both the basic and applied points of view.

Details pertinent to materials and experimental procedures used appear elsewhere (11). We briefly note, regarding procedures, that surfaces of carbon specimens were bombarded with actinide ions, heated in vacuum, then assayed for diffused material either during or after precision polishing operations. The data are plotted in the form of fraction of diffused material remaining after polishing versus distance removed by polishing. These plots are compared to plots of the applicable function, $\text{erfc}(\underline{u})$ vs $\underline{u}$, and coefficients are thus extracted from the data. An apparent initial profile, observed in several blank experiments, is accounted for by pretending that some diffusion occurred prior to the actual diffusion anneal. Thus initially, $\underline{u}$ is given by $(\underline{x})/(4Dt)_0^{\frac{1}{2}}$, where $(4Dt)_0 = 7.0 \times 10^{-7} \text{ cm}^2$, and finally by $(\underline{x})/[(4Dt)_0 + (4Dt)]^{\frac{1}{2}}$, where $D \text{ cm}^2/\text{sec}$ is the coefficient sought.

Results pertinent to migration in a direction perpendicular to the deposition planes are shown in Fig. 16 for thorium and Fig. 17 for protactinium. In both cases the assay for diffused material was based on gamma counting of Pa^{233} activity produced by neutron activation of thorium. Activation was performed after diffusion heating for the thorium experiments, but prior to diffusion heating for the protactinium experiments (wherein the amount of the protactinium was minute compared to the amount of thorium present). It turned out that the perpendicular migration characteristics of thorium and protactinium were the same. Furthermore, the migration could be called a diffusion process since the complementary error function gave a reasonable description of the experimentally observed behavior.

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Fig. 17. Diffusion Results for Protactinium in Pyrolytic Carbon with Migration Perpendicular to the Deposition Plane. The initial actinide content was $29 \mu\text{g Th/cm}^2$ specimen surface.

Experiments designed to study parallel migration characteristics produced results that were quite different from those given in Figs. 16 and 17. When the diffusion equation was followed, as shown in Fig. 18, the penetrations were much greater in the parallel direction than in the perpendicular direction and it is obvious that the diffusion rates followed the same trend. It should be clearly stated, however, that the results given in Fig. 18 represent a minority of the parallel-direction results. In most cases the curves were straight lines and could not be correlated on the basis of diffusion relationships. The same anomaly has been observed by Wolfe (12), who is engaged in similar work elsewhere; this investigator shares our suspicion that the straight lines result from the existence of microcracks which propagate along the basal sheets (as partially verified by autoradiographic and microscopic studies).

Only a few points were available for each uranium experiment tabulated in Fig. 18, because employment of the activation gamma-counting procedures required the use of fission products as a basis for the measurements. To eliminate possible contributions of fission recoils, the assays were performed on large prepolished segments of the specimens. This approach precluded the acquisition of complete penetration curves for uranium. Pure U^{235} was used in the source layer to enhance the fission-product activity level. Comparisons of the uranium and protactinium results of Fig. 18 indicate, once again, that two different members of the actinide series exhibit the same diffusion characteristics for a given diffusion direction. All of the results given in Figs. 16, 17, and 18 are summarized in Fig. 19 in terms of a $\log D$ vs $(T)^{-1}$ plot as well as some previously reported (11) results for a porous graphite.

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Fig. 18. Diffusion Results for Uranium and Protactinium in Pyrolytic Carbon with Migration Parallel to the Deposition Plane. The initial actinide concentration was $29 \mu\text{g Th and/or U/cm}^2$ specimen surface.

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Fig. 19. Actinide Diffusion Coefficients as a Function of Temperature. The porous graphite curve is based on the results of instantaneous-source-layer experiments with thorium and constant-potential experiments with uranium.

At this stage of the investigation, major attention has been focused on the magnitudes of the coefficients rather than activation energies. Nevertheless, we note that the energy of activation associated with the results shown on Fig. 19 for diffusion of actinide in both the parallel and the perpendicular directions is 61 kcal/mole. This represents only half the value cited by Borg et al., (13) for uranium (and more recently, thorium) in a pyrographite. On the other hand, the energy of activation for the present work shows reasonable agreement with values cited by Wolfe (14) for silver and nickel in a pyrographite. A positive explanation for the apparent discrepancy between the two sets of actinide data is yet to be attained; however, it is recognized that the actinide concentrations in Borg's experiment were considerably lower than the concentrations involved in the present work.

It is pertinent to mention at this point that the present studies are actually auxiliary groundwork for the more difficult constant-potential diffusion studies, wherein the graphite is exposed to pure actinide carbide in a fashion analogous to coatings on fuel particles. For this reason, the present experiments were designed to employ the maximum actinide concentration that would be compatible with boundary conditions associated with the diffusion relationship. The best evaluation of the present results from this standpoint might be gained through a comparison with earlier investigations of Loftness (15) and Loch (16) which involved uranium carbide in contact with porous graphites. We note, therefore, that both the magnitude of the coefficients and activation energies for our companion porous graphite experiments show

good agreement with earlier work which involved high actinide concentrations. Constant-potential experiments for both pyrolytic carbon and porous graphite (17, 18) are under way.

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