~~CONFIDENTIAL~~

MASTER

UNCLASSIFIED

U

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California

LOS ALAMOS • NEW MEXICO

Development of Particles Coated with
Pyrolytic Carbon
IX. Studies of Commercial Experimental
Coated Particles (U)

Classification cancelled (or changed to)

by authority of Docby R.F.C. T/C, date AUG 29 1973

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

AEC RESEARCH AND DEVELOPMENT REPORT

This report contains no defense information other than Restricted
Data and is releasable through the ~~Dissemination~~ Program

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its trans-
mittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

Group 1 - Excluded from automatic downgrading and declassification

UNCLASSIFIED

~~CONFIDENTIAL~~DISTRIBUTION OF THIS DOCUMENT IS LIMITED
to Government Agencies and their Contractors + C&E

~~CONFIDENTIAL~~

Written: November 1970

Distributed: January 1971

LA-4560

C-91, NUCLEAR REACTORS
FOR ROCKET PROPULSION
M-3679 (64th Ed.)

UNCLASSIFIED

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Development of Particles Coated with
Pyrolytic Carbon
IX. Studies of Commercial Experimental
Coated Particles (U)

by

H. R. Baxman
J. P. Bertino
R. J. Bard
S. W. Hayter
J. A. O'Rourke
L. S. Levinson

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

would not infringe privately owned rights.

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

UNCLASSIFIED
RESTRICTED DATA

This document contains information which is defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any form to an unauthorized person is prohibited.

Group 1 and 2 information is exempt from automatic downgrading and declassification

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONFIDENTIAL

TABLE OF CONTENTS

	Page
Abstract	1
1. Introduction	1
2. Materials, Equipment, and Experimental Methods	2
2.1 Materials	2
2.1.1 Coated Particles and UC ₂ Cores	2
2.1.2 Cases	2
2.2 Coating Equipment and Procedures	2
2.3 Evaluation Procedures	3
3. Studies of Commercial Experimental Coated Particles	4
3.1 Particles with Single-Layer Coatings	4
3.2 Particles with Two-Layer Coatings	8
3.3 Electron Microscopy of Oriented Pyrolytic Carbons	9
4. Summary	15
Acknowledgments	15
References	16
Appendix A. Specifications for Experimental Coated Particles	17
Appendix B. Determination of Preferred Orientations of Pyrolytic Carbons at IASL and General Atomic	19

LIST OF TABLES

I. Properties of UC ₂ Cores	2
II. Properties of High-Density, Oriented Pyrolytic Carbons	6
III. Test Results on Particles with Single-Layer Coatings on General Atomic UC ₂ Cores	7
IV. Results of Testing for Core Damage during Fluidization at 1200°C before Coating	8
V. Test Results on Particles with IASL Two-Layer Pyrolytic Carbon Coatings on 124- to 175-μ-diam General Atomic Experimental UC ₂ Cores	9
VI. Test Results on Experimental Particles Coated by General Atomic and IASL	10
VII. Results of Cyclic Testing of Coated Particles	12

DEVELOPMENT OF PARTICLES COATED WITH PYROLYTIC CARBON.

IX. STUDIES OF COMMERCIAL EXPERIMENTAL COATED PARTICLES.

by

H. R. Bowman, J. P. Bertino, R. J. Bard,
S. W. Hayter, J. A. O'Rourke, L. S. Levinson

ABSTRACT

Attempts made through 1968 to obtain kilogram quantities of improved particles having General Atomic UC_2 cores with a complete graphite shell and having pyrolytic carbon coatings of the types developed at the Los Alamos Scientific Laboratory (LASL) are described. Particles with single- and two-layer coatings were purchased for use in developmental Rover fuel elements. The experimental particles coated in production equipment at General Atomic were substantially less stable at 2500°C and higher temperatures than control particles with the same cores coated in 1-in.-diam equipment at LASL. The high-density, oriented pyrolytic carbon deposited at LASL with a smooth microstructure was proved to be more resistant to penetration by melt than the high-density, oriented pyrolytic carbon deposited at General Atomic with an "onionring" type of microstructure. Electron microscopy indicated that the deficiencies of the General Atomic coating were due to incorporated soot that blocked densification of the coating during pretreatment of the particles and led to persistent disordered regions with poor resistance to penetration by melt.

1. INTRODUCTION

Fuel elements for Rover reactors tested through 1970 contained pyrolytic-carbon-coated UC_2 particles in a graphite matrix. The pyrolytic carbon (PyC) protected the UC_2 from reaction with gases during and after fabrication. Coated particles made practical the coating of the gas passage holes in the UC_2 -loaded graphite with metal carbides by chemical vapor deposition from mixtures containing metal halides and resulted in a finished fuel element with good shelf stability. Small coated particles with high uranium content were required because of the thin webs in the 19-hole fuel element geometry and the high uranium loadings. Production particles with nominal 50- to 150- μ -diam UC_2 cores with 25 $\pm$ 5- μ -thick PyC coatings were used.

Coated particles that could be heated at 2500°C for at least 4 h without penetration of the PyC coatings by migration (attack of the PyC by the UC_2) were required to withstand the temperatures used in

fuel element manufacture. Such particles became available on a routine production basis in 1964 from several commercial sources. The goal of Rover fuel particle work then became the development of PyC-coated particles that would be stable at reactor operating temperatures of 2500°C and above for at least 30 min.

Most of the development of improved Rover fuel particles since 1967 has been done at the Los Alamos Scientific Laboratory (LASL). The work has been concentrated on developing resistant PyC coatings for use on a unique type of UC_2 core with a complete graphite shell manufactured by General Atomic* by a proprietary process, obtaining improved UC_2 cores from General Atomic, preparing and studying improved core-coat combinations, and attempting to obtain

* General Atomic became Gulf General Atomic in late 1967. Particles described in this report were purchased before and after that date. The company will be referred to as General Atomic in this report.

practical quantities of improved coated particles for use in developmental fuel elements. This report, which is the ninth in a series of summary reports on work done at LASL on the development of particles coated with pyrolytic carbon, describes LASL studies of commercial experimental coated particles purchased from General Atomic through 1968. Interim reports of the work were given at several meetings of the AEC Coated Particle Fuels Working Group.¹⁻³ Previous summary reports in the series describe studies with coatings deposited from methane at low temperatures (1200, 1300, and 1400°C),⁴ from methane at high temperatures (1700, 2000, and 2300°C),⁵ from acetylene at low temperatures (1200 and 1400°C),⁶ and from a variety of hydrocarbons at low temperatures (up to 1400°C),^{7,8} studies with doped coatings,⁹ comparisons of experimental UC₂ cores,¹⁰ studies of porous carbon,¹¹ and studies of improved core-coat combinations.¹² LASL work on ZrC-coated UC-ZrC particles has also been reported.¹³ Subsequent summary reports will describe LASL work on scaling up laboratory developments and on other aspects of the Rover fuel particle problem.

2. MATERIALS, EQUIPMENT, AND EXPERIMENTAL METHODS

2.1 Materials

2.1.1 Coated Particles and UC₂ Cores

Experimental PyC-coated UC₂ particles containing 93%-enriched uranium were purchased from General Atomic on a fixed-price, best-efforts basis to conform to LASL specifications. Samples of UC₂ cores representative of those in the coated particles were also purchased in every case for coating at LASL to obtain a comparison with the particles coated by General Atomic.

The General Atomic type of UC₂ core has a complete graphite shell that, if not extensively damaged before or during coating, prevents migration of UC₂ into any type of PyC coating in testing up to at least 2300°C for at least 4 h. X-ray diffraction by intact General Atomic cores of several earlier batches (GA-210-ECR and GA-IUC-1) had shown tetragonal UC₂ and two distinct crystalline carbon components of very large crystallite size, one with nearly perfect graphite stacking and the other almost completely turbostratic. The turbostratic component was about 10% of the total crystalline carbon. Fragments of the graphite shells, the residue from leaching crushed particles with nitric acid solution, had a

density of 2.24 g/cm³ by the sink-float method.

Properties of some of the batches of cores described in this report are given in Table I.

2.1.2 Gases

Methane or acetylene was used for the deposition of PyC coatings at LASL. The methane was Phillips CP grade, which typically analyzed 99% CH₄, 0.1 to 0.2% C₂H₆, a trace of C₃H₈, and up to 1.0% N₂, CO, and CO₂. The acetylene was metered from the tanks in which it was dissolved in acetone and thus contained up to several percent acetone impurity. Tank helium was used without purification as the diluent in coating gas mixtures.

2.2 Coating Equipment and Procedures

The 1-in.-i.d. graphite coater shown in Fig. 1 was used for the deposition of PyC on fluidized beds of particles at LASL. The design permitted disassembly and cleaning after each run. The coater was heated by a Globar resistance furnace. A helium sweep between the mullite sheath and the coater protected the graphite from oxidation. The base section was not cooled, permitting good uniformity of temperature in the coater. Beds of UC₂ particles with diameters greater than 100 μ fluidized with 2.63 l (STP)/min of helium were localized in the coating chamber and had temperatures measured with a thermocouple probe inserted from above that were not more than about 20° above the nominal temperature of 1200°C. The power to the furnace was adjusted to compensate for the heat effects from the decomposition of the hydrocarbon and to keep the temperature of the reference thermocouple constant at a predetermined value corresponding to the desired temperature at the base of the cone. The gas was preheated in

Table I
Properties of UC₂ Cores

Property	Batch No.		
	GA-210-ECR	GA-210-ECR	GA-IUC-1
Uranium content, wt %	88.6	89.4	89.5
Total carbon content, wt % ^a	11.3	10.5	10.4
Oxygen content, ppm	140	190	150
Nitrogen content, ppm	47	120	290
Spec. impurities, ppm - Fe	20	50	50
- Si	15	5	5
- other > 25	--	--	40-81
Particle density, g/cm ³	10.13	10.46	10.71
Particle size, μ ^b	124-175	104-147	104-147
Enrichment in ²³⁵ U, %	93	93	93
Uranium leached, % of total ^c	18	24	31

^aBy difference.

^b Tyler sieve range.

^c In HNO₃ at 95°C for 8 h.

CONFIDENTIAL

the 3/32-in.-diam inlet passage, but the residence time per unit length in the inlet passage was only about 1/100 of that in the fluidized bed. The effective contact time was not influenced significantly by preheating. Coatings were deposited on fluidized beds with surface areas that corresponded to an initial surface area of 1100 cm² of the UC₂ cores.

The coater was operated at the ambient pressure of about 580 Torr at Los Alamos (elevation 7200 ft). For this reason, gas flows are expressed in liters (STP)/min. The input hydrocarbon partial pressures corresponding to concentrations given in this report are lower than those at most other coating laboratories by a factor of about 580/760.

2.3 Evaluation Procedures

Samples were split by using multichute rifflers. Routinely, the coated particles were micro-radiographed for determination of coating uniformity and thickness, and a metallographic section was made for examination of the microstructures. The thickness of the graphite shell on the core and the

thicknesses of the layers of PyC in multilayer coatings were determined by measuring the relative thicknesses on particles sectioned near the midplane and by normalizing these values to the average total thickness measured on a microradiograph (a close enough approximation for particles sectioned near the midplane). Properties of the pyrolytic carbons were measured on monolithic deposits on particles and disks that were coated simultaneously in fluidized beds. (The disks were used to obtain wafers of PyC for the measurement of the preferred orientation by x-ray diffraction, according to the method of Bokros.¹⁴) Detailed descriptions of the standard procedures and equipment used at IASL for evaluating coated particles and PyC coatings are given elsewhere.⁴

The thermal stability of coated particles was determined by heating the loose particles in a graphite crucible, leaching the heated particles and the crucible in 8 N HNO₃ at 95°C for 8 h, and analyzing the leach solution for uranium by the colorimetric method. The following types of heat treatments were used routinely: (1) direct testing at 2500°C for 30 min (Test I) to provide base data for determining the effects of pretreatment at lower temperatures, and (2) pretreatment at 2300°C for 4 h, cooling to room temperature, and then heating at 2500 or 2600°C for 30 min (Tests II or III) to simulate the "2300°C" exposure of particles in the "graphitizing" step of fuel element manufacture and eventual higher temperature exposure in reactor operation (but not including the exposures below 2300°C that coated particles in fuel elements receive in the postmachining HCl leaching and metal carbide coating steps of fuel element manufacture). Some of the better particles coated at IASL were tested at 2700 or 2800°C for 30 min following pretreatment at 2300°C for 4 h and cooling (Tests VI or VII). Also, many batches of particles were tested with three cycles to 2500 or 2600°C for 30 min plus cooling, following pretreatment at 2300°C for 4 h plus cooling, designated as Tests II(3) or III(3). In all these tests, the coated particles were heated in contact with one another, rather than separated as in a graphite matrix, with the result that the leach values gave the most pessimistic evaluation of performance because of the possibility of attack from the outside by the melt from particles with penetrated coatings.

Fig. 1. Low-temperature graphite coater.

3. STUDIES OF COMMERCIAL EXPERIMENTAL COATED PARTICLES

Extensive work at IASL had indicated that PyC-coated UC₂ particles with adequate stability at 2500°C could not be obtained if the coating thickness were limited to about 25 μ , even when General Atomic experimental UC₂ cores were used.¹⁰ Subsequent studies were concentrated on particles with nominal 40- μ -thick coatings on 104- to 147- μ -diam cores or nominal 50- μ -thick coatings on 124- to 175- μ -diam cores.¹² (These coat-thickness, core-size combinations were chosen as the best compromises among uranium content, coat thickness, and particle size.) The development of improved PyC coatings at IASL proceeded concurrently with the preparation of better experimental UC₂ cores by General Atomic.¹² Attempts were made several times during this period to obtain kilogram quantities of improved coated particles from General Atomic for use in developmental fuel elements.

Experimental PyC-coated UC₂ particles were purchased from General Atomic on a fixed-price, best-efforts basis to conform to IASL specifications. The specifications called for the UC₂ cores to be made the same way as specific previous batches and for the PyC coatings to have physical properties similar to those of coatings developed at IASL. Samples of UC₂ cores representative of those in the coated particles were obtained and coated at IASL to correlate performances of the coated particles with the preparation of the coatings in production equipment at General Atomic and in laboratory equipment at IASL. Such comparisons uncovered substantial improvements in the quality of the General Atomic experimental UC₂ cores and important differences in the pyrolytic carbons deposited in the different types of equipment.

3.1 Particles with Single-Layer Coatings

High-density, laminar PyC deposited at low temperature (1200°C) was shown at IASL in 1963 to be resistant to UC₂ migration at 2300°C.¹⁵ The oriented character of such PyC was established in 1964 by General Atomic workers.¹⁶ Suitably thin single-layer coatings of high-density, oriented PyC were shown to be inadequate for containing melt at 2500°C or above in particles having the best General Atomic UC₂ cores available through 1966.^{17,18,10} However, such coatings on either experimental or routine-

production General Atomic UC₂ cores did provide substantial improvement in thermal stability over the General Atomic production PyC coating.

In early 1967, IASL purchased two nominal 1-kg batches of experimental PyC-coated UC₂ particles from General Atomic, along with nominal 200-g samples of the corresponding UC₂ cores. One batch of particles (GA-XEK-4444) was purchased on a specification calling for a nominal 40- μ -thick, single-layer coating on 104- to 147- μ -diam General Atomic production cores with at least 10.2 wt % carbon. (See Specification CMB-8-4234 in Appendix A.) The other batch (GA-XEK-4420) was purchased on a specification calling for a nominal 50- μ -thick, single-layer coating on 124- to 175- μ -diam General Atomic experimental cores made like preceding batches GA-1370ES¹⁰ and GA-266¹⁰⁻¹² and containing 11.0 $\pm$ 0.2 wt % carbon. (See Specification CMB-8-4224 in Appendix A.) A low-temperature PyC coating with density 2.00 to 2.12 g/cm³ and Bacon anisotropy factor of at least 12 was specified for each batch.

The coating deposited on these batches in General Atomic production-scale equipment was an "onionring" variety of the oriented laminar type, whereas the oriented laminar coating deposited at IASL in laboratory-scale equipment was a smooth variety. Photomicrographs of these two varieties are shown in Fig. 2.

Only one of the three coated disks supplied with Batch GA-XEK-4444 had a coating that matched the particle coatings in both microstructure and thickness. The properties of a wafer of PyC removed from that disk and of fragments of the particle coatings were determined before and after heating at 2300°C for 4 h. The results are given in Table II along with those for the corresponding IASL PyC. The properties of the PyC deposited by General Atomic on Batch GA-XEK-4444 were very similar to those of the IASL-deposited PyC, but the General Atomic PyC did not densify as well at 2300°C. Also, the General Atomic PyC did not densify, recrystallize, or order as much as the IASL PyC when fragments of the particle coatings were heated at 2800°C for 30 min after pretreatment at 2300°C for 4 h and cooling. None of the three coated disks supplied with Batch GA-XEK-4420 had a coating that matched the particle coatings in thickness.

Table II
Properties of High-Density, Oriented Pyrolytic Carbons

Deposited By	PyC Sample	Heat Treatment	Properties			
			Density, ^a g/cm ³	Apparent Crystallite Size (L _c), Å	Interplanar Spacing (d ₀₀₁), Å	Preferred Orientation ^b M BAF
IASL ^c	From particles	None	2.06	34	3.15	-- --
		2300°C - 4 h	2.18	178	3.41	-- --
		2300°C - 4 h + cooling + 2800°C - 30 min	2.25	~ 900	3.37	-- --
	From disk	None	2.09	39	3.45	12-14 --
		2300°C - 4 h	2.22 ^e	580	3.385	> 19> > 120
General Atomic ^d	From particles	None	2.04	56	3.46	-- --
		2300°C - 4 h	2.12 ^f	156	3.39	-- --
		2300°C - 4 h + cooling + 2800°C - 30 min	2.17	235	3.382	-- --
	From disk	None	2.07	40	3.45	16-17 16.4
		2300°C - 4 h	2.18 ^e	1100	3.390	200-230 120

^aDensities of the coating fragments from the particles before heating were measured by both the sink-float and mercury-displacement methods. Densities of all other samples were measured by the sink-float method only.

^bM determined by fitting $I(\theta) = \cos^4 \theta$ to the corrected $I(\theta)$ vs θ x-ray diffraction reflection data. BAF = Bacon anisotropy factor obtained from x-ray diffraction reflection data for highly oriented specimens for which the intensity had dropped to background at $\theta \leq 50^\circ$, assuming no contribution at higher angles.

^cIASL standard high-density, oriented PyC. Data are for Batches GA-266-5, C-9 and GA-266-9, C-1 (see Table VI of Ref. 12). This type of coating was deposited at average rates of 6 to 8 μ /h in a 1-in.-diam graphite coater at 1200°C from 40% methane-60% helium at an input flow rate of 2.63 l(STP)/min on fluidized beds with an initial surface area of 1100 cm².

^dData are for Batch GA-XEK-4444 coated by General Atomic in production-scale equipment.

^eThe heated disks had to be crushed before density measurement because they were puffed up from internal delaminations.

^fRange 2.10 to 2.14 g/cm³.

ences between Batches GA-4420ES, C-1 and GA-XEK-4420.

It was concluded from the above observations that the smooth variety of high-density, oriented PyC deposited by IASL in laboratory-scale equipment had better resistance to attack by melt than the "onionring" variety deposited by General Atomic in production-scale equipment.

In late 1967, 20 kg U of coated particles with nominal 40- μ -thick, single-layer coatings on 104- to 147- μ -diam General Atomic production cores were purchased for use in special developmental fuel elements for the Pewee-1 Reactor. (See Specification GMB-8-4234, revised December 8, 1967, in Appendix A.) This type of coated particle represented a substantial improvement in stability over the standard Rover coated particles in 30-min tests at 2500 or 2600°C (compare Batches GA-XEK-4444 and GA-E-LY-121 in Table III) and was purchased at that time because of the pressing schedule for the fabrication of Pewee-1 fuel elements and the lack of time to bring to the specification stage more advanced particles being developed at IASL with two-layer coatings on General Atomic experimental UC₂ cores. Also, the additional stability obtained up to that time with a single-layer coating deposited by General Atomic on experimental UC₂ cores did not appear to warrant the extra

expense of the experimental cores (compare Batches GA-XEK-4420 and GA-XEK-4444 in Table III).

The coated particles were received as eight separate coater batches, four of which had very similar histories and four of which differed from the others and each other because of variations in the conditions of preparation. All the batches had the "onionring" variety of oriented coating. The four similar batches were combined into a crossblend from which particles were split for the fabrication of special developmental fuel elements for Pewee-1. The stabilities of the particles of the crossblend and of the corresponding IASL-coated comparison particles (Crossblend GA-EB-36.00 and Batch GA-EB-36.00ES, C-3, respectively, in Table III) were about as expected. Again, the IASL-deposited coating was somewhat more resistant and densified more at 2300°C than the coating deposited by General Atomic. Each of the three coated graphite disks supplied with each of the four component batches of the crossblend was examined at IASL, and in all cases the PyC deposit on the disk was found to be different from the particle coating. The particle coatings were the "onionring" variety of the oriented laminar type, whereas the disk coatings were a smooth variety and much thinner. Because of this lack of correspondence

Table III

Test Results on Particles with Single-Layer Coatings
on General Atomic UC₂ Cores

Diam Range, μ	Core Graphite Shell Thickness, μ^a	Coated Particle Batch No.	Particles Coated By	Average Crushing Strength, lb	Average Coating Thickness, μ^b	% U Exposed by Heat Treatment ^{c,d}		
						I	II	III
53-147	2.2	GA-E-LY-121 ^{e,m}	GA	(0.7)	23	82	76	92
104-147	2.0	GA-XEK-4444 ^f	GA	1.5	45	20	14	31
		GA-4444ES,C-1 ^g	LASL	--	39	26	13	21
124-175	3.0	GA-XEK-4420 ^{h,m}	GA	1.5	49	7-8	4-5	10-13
		GA-4420ES,C-11 ^{h,m}	LASL	--	50	1.9-2.9	0.4-0.5	1.4-2.3
		GA-4420ES,C-7 ^j	LASL	--	48	4	0.8	4
104-147	2.0	GA-EB-36.00 ^{k,m}	GA	1.4	39	30	16	33
		GA-EB-36.00ES,C-3 ^{l,m}	LASL	--	38	21	11	23

^aAverage value for 25 particles in a metallographic mount, normalized to the midplanes of the particles.

^bThe values do not include the graphite shells on the cores.

^cI = 2500°C - 30 min; II = 2500°C - 4 h + cooling + 2500°C - 30 min; III = 2500°C - 4 h + cooling + 2600°C - 30 min.

^dDetermined by leaching the heated particles and the crucible in 9 N HNO₃ at 95°C for 8 h and analyzing the leach solution for U. Values are averages of duplicate samples heated separately at 2500 or 2600°C. Where two values are given, two separate test series were run.

^eBest shipment lot of standard production coated particles received on LASL Purchase Order LA6-00050.

^fOne-kg trial batch with production cores. LASL Purchase Order LA7-41717. See Table II for properties of the PyC coating.

^gParticles with LASL-deposited high-density, oriented PyC coating and cores representative of those used for Batch GA-XEK-4444 coated particles. See Table II for properties of this type of LASL resistant PyC coating.

^hOne-kg trial batch with experimental cores. LASL Purchase Order LA7-41717.

ⁱParticles with LASL-deposited high-density, oriented PyC coating and cores representative of those used for Batch GA-XEK-4420 coated particles. See Table II for properties of this type of LASL resistant PyC coating.

^jCoated as was Batch GA-4420ES,C-1, except that the bare cores were fluidized in helium for 15 min, instead of the usual 1 min, before the start of PyC deposition.

^kEleven-kg crossblend of four nominal 3-kg batches with production cores (Batches C-4002EK, C-4003EK, C-4004EK, and C-4008EK). LASL Purchase Order LA7-41717-1. Some of these particles were used to make special fuel elements for the Fwese-1 Reactor.

^lParticles with LASL-deposited high-density, oriented PyC coating and cores representative of those used for the component batches of Crossblend GA-EB-36.00.

^mProperties of fragments of the particle coatings for the various batches were:

Batch No.	Condition of Fragments	Density, g/cm ³	Apparent Crystallite Size (L _c), Å	Interplanar Spacing (d ₀₂₀), Å
GA-E-LY-121	Before heating	1.89	32	3.45
	After 2500°C - 4 h	1.96	73	3.44
GA-XEK-4420	Before heating	2.03	32	3.46
	After 2500°C - 4 h	2.11	135	3.40
GA-4420ES,C-1	Before heating	2.08	36	3.46
	After 2500°C - 4 h	2.20	223	3.40
GA-EB-36.00	Before heating	2.00	33	3.45
	After 2500°C - 4 h	2.11	136	3.40
GA-EB-36.00ES,C-3	Before heating	2.07	35	3.46
	After 2500°C - 4 h	2.19	205	3.39

Table IV

Results of Testing for Core Damage during Fluidization at 1200°C before Coating^a

Batch No.	Fluidization Time, min	% U Leached		
		Sample 1	Sample 2	Average
GA-4420ES	0 (Control)	21.6	23.1	22
	1	31.9	32.0	32
	15	37.4	38.1	38

^a Individual 1/4-g samples of cores (except the control samples) were dropped into a 1-in.-diam graphite coater at 1200°C with 2.63 l(STF)/min of helium flowing, fluidized for the indicated time, and then dropped into a helium-filled receiver. The samples were leached in 8 N HNO₃ at 95°C for 8 h, and the leach solutions were analyzed for uranium.

between disk and particle coatings, the preferred orientations of the coatings deposited by General Atomic on this order could not be measured.

The particles of Crossblend GA-EB-36.00 were referred to as "big beads" at LASL because they had an average particle size that was 2 mils larger and a maximum particle size that was 1 mil larger than the corresponding values for standard Rover coated particles. The use of the particles of Crossblend GA-EB-36.00 in fuel elements for the Pewee-1 Reactor is described in detail elsewhere.¹⁹

3.2 Particles with Two-Layer Coatings

The General Atomic experimental UC₂ cores of Batch GA-4420ES described above were substantially better than those of preceding Batch GA-266. For this reason, two additional 1-kg batches of experimental UC₂ cores were purchased from General Atomic in early 1968. These cores (Batches GA-F-300LES and GA-G-300LES) were the best ever made by General Atomic. In addition, a very effective two-layer coating with an inner sacrificial layer of high-density, isotropic PyC and an outer resistant layer of high-density, oriented PyC with a smooth microstructure was developed at LASL in early 1968. This type of PyC coating on the best General Atomic experimental UC₂ cores led to particles with exceptional stability at temperatures up to 2800°C for short times. The progressive improvement of coated particles containing General Atomic experimental UC₂ cores and having the LASL-deposited two-layer PyC coating is illustrated in Table V.

The above improvements led to the hope that

coated particles could be produced in quantity that would be substantially more stable than those purchased previously. Consequently, in 1968 another 10 kg U of experimental coated particles were purchased from General Atomic. The coatings were specified to have an inner layer of high-density, isotropic PyC with density 1.90 to 1.95 g/cm³ and an outer layer of high-density, oriented PyC with density 2.00 to 2.12 g/cm³ and Bacon anisotropy factor of at least 12, and the UC₂ cores were specified to be made like experimental Batches GA-4420ES and GA-F-300LES (see Appendix A for Specification GMB-8-4335 for particles with a nominal 50-μ-thick coating on 124- to 175-μ-diam cores, and Specification GMB-8-4363 for particles with a nominal 40-μ-thick coating on 104- to 147-μ-diam cores). Three batches of the large-core, thick-coat particles, about 2.4 kg U each, and one batch of the smaller-core, thinner-coat particles, 2.3 kg U, were obtained. Corresponding uncoated UC₂ particles, corresponding particles with only the sacrificial layer, and graphite disks coated in fluidized beds of the particles were also obtained.

The properties and test results for these particles (Batches GA-W-329, -331, -332, and -330) are given in Table VI. Photomicrographs and microradiographs of particles from two of the batches are shown in Fig. 3. The inner layer of PyC varied from isotropic (Batch GA-W-329) to somewhat oriented (Batches GA-W-331, -332, -330) in appearance under polarized light and were all high density (1.9 to 2.0 g/cm³). (The inner layer of Batch GA-W-330 had the highest density and appeared to be the most oriented.) The outer layers were all the "onionring" variety of oriented laminar PyC. For a given core-size, coat-thickness combination, these particles were the best obtained to date from General Atomic. (Compare Batches GA-W-329, -331, and -332 with Batch GA-XEK-4420 in Table III, and Batch GA-W-330 with Batches GA-XEK-4444 and GA-EB-36.00 in Table III.) However, the performances fell far short of the best of the LASL-coated particles with the best of the General Atomic experimental UC₂ cores (Table V).

A direct comparison of the LASL and General Atomic high-density, oriented pyrolytic carbons was obtained by comparing the stabilities of the above particles with two-layer coatings deposited by General Atomic, corresponding particles with the inner layer deposited by General Atomic and the outer layer

Table V

Test Results on Particles with IASL Two-Layer Pyrolytic Carbon Coatings
on 124- to 175- μ -diam General Atomic Experimental UC₂ Cores

Year Purchased	Core		Coating Batch No.	Coating Thickness, μ			% U Exposed by Heat Treatment ^{d,e}				
	Graphite Shell Thickness, μ^a	Batch No.		Inner HDI ^b	Outer HDO ^c	Total Coat	I	II	III	VI	VII
1966	3.0	GA-266-5 ^f	C-19A	17	31	48	7	1.2	4	--	--
1967	3.0	GA-4420ES ^g	C-6A	18	32	50	1.5	0.3	1	4	8
1968	3.1	GA-F-300LES-5 ^h	C-1A	17	32	49	1.7	0.07	0.13	1.0	2.5
	3.2	GA-G-300LES-5 ^h	C-1A	17	33	50	4	0.07	0.2	0.9	2.1

^aAverage value for 25 particles in a metallographic mount, normalized to the midplanes of the particles.

^bHDI = IASL standard high-density, isotropic PyC with density ρ about 1.9 g/cm³ and preferred orientation index $M < 0.1$. (This type of coating was deposited at average rates of about 140 μ /h in a 1-in.-diam graphite coater at 1200°C from 40% acetylene-60% helium at an input flow rate of 2.63 l(STP)/min on fluidized beds with an initial surface area of 1100 cm². See Table XXVI of Ref. 12 for further properties.)

^cHDO = IASL standard high-density, oriented PyC. See Table II for preparation and properties.

^dI = 2500°C - 30 min.

VI = 2300°C - 4 h + cooling + 2700°C - 30 min.

II = 2300°C - 4 h + cooling + 2500°C - 30 min.

VII = 2300°C - 4 h + cooling + 2800°C - 30 min.

III = 2300°C - 4 h + cooling + 2600°C - 30 min.

^eDetermined by leaching the heated particles and the crucible in 8 N HNO₃ at 95°C for 3 h and analyzing the leach solution for uranium. Values are averages of duplicate samples heated separately at 2500°C or above.

^fIASL Purchase Order LA6-00050-1.

^gIASL Purchase Order LA7-41717.

^hIASL Purchase Order LA7-41717-1.

by IASL, and corresponding particles with both layers deposited by IASL. The results of testing these particles are given in Table VI. The relative effectiveness of the sacrificial layers deposited by General Atomic and IASL varied from batch to batch, with the PyC deposited by General Atomic more effective in two batches and the IASL-deposited PyC more effective in the other two. The greater effectiveness of the IASL-deposited high-density, oriented PyC with a smooth microstructure was clearly shown; particles with the outer layer deposited at IASL over inner layers deposited by either General Atomic or IASL performed better than particles with both layers deposited by General Atomic.

The differences between the high-density, oriented pyrolytic carbons deposited by IASL and by General Atomic were accentuated by cyclic testing for longer times at 2500 or 2600°C. Table VII shows results of cyclic testing of a variety of coated particles, including all experimental coated particles from General Atomic described in this report. All of the latter particles performed very poorly when heated for three 30-min cycles at 2500 or 2600°C following pretreatment at 2300°C for 4 h and cooling.

Other work has shown that the effect of time at temperature is more important than the effect of cycling.¹²

3.3 Electron Microscopy of Oriented Pyrolytic Carbons

It was suspected that the difference between the smooth microstructure of the high-density, oriented PyC deposited in 1-in.-diam coaters at IASL and the "onionring" type of microstructure of the high-density, oriented PyC deposited in production equipment at General Atomic was due to the periodic incorporation of soot particles into the latter coating. This suspicion was based on the mechanism of Browning and coworkers,²⁰ who proposed that laminar structures are formed during pyrolytic carbon deposition in fluidized beds as a result of periodic interruptions in the overall growth pattern by the accretion of soot and who in fact observed that the return of loose soot to the fluidized bed by artificial means made the laminar structure more predominant. The two types of PyC were examined by electron microscopy in an attempt to establish the reasons for the differences between the two microstructures.

Table VI

Test Results on Experimental Particles
Coated by General Atomic and IASL^a

Core			Coated Particle Batch No.	Coated By		Coating Thickness, μ			% U Exposed by Heat Treatment ^{f,g}	
Diam Range, μ	Carbon ^b Content, wt %	Graphite Shell Thickness, μ^c		Inner Layer ^d	Outer Layer ^e	Inner Layer	Outer Layer	Total	II	III
124-175	11.3	4.2	GA-W-329	GA	GA	15	35	50	2.4	5
			GA-W-329I, C-1A ^h	GA	IASL	14	35	49	0.7	2
			GA-W-329ES, C-1A	IASL	IASL	16	33	49	0.1	0.9
	11.2	3.4	GA-W-331	GA	GA	15	31	46	1.1	4
			GA-W-331I, C-1A ^h	GA	IASL	15	30	45	0.2	0.6
			GA-W-331ES, C-1A	IASL	IASL	14	32	46	0.24	1.2
	11.0	3.1	GA-W-332	GA	GA	17	29	46	1.0	4
			GA-W-332I, C-2A ^{h,i}	GA	IASL	17	28	45	1.0	2.0
			GA-W-332ES, C-1A	IASL	IASL	15	32	47	0.5	1.2
104-147	11.8	3.5	GA-W-330	GA	GA	9	26	35	5	11
			GA-W-330I, C-1A ^h	GA	IASL	9	27	36	0.4	1.1
			GA-W-330ES, C-1A	IASL	IASL	9	25	34	0.7	2

^aIASL Purchase Order LA7-41717-1.^bGeneral Atomic values.^cAverage value for 25 particles in a metallographic mount, normalized to the midplanes of the particles.^dThe GA inner layers were a variety of high-density (1.9 to 2.0 g/cm³) isotropic or slightly oriented pyrolytic carbons. The IASL inner layers were the IASL standard isotropic PyC of density about 1.9 g/cm³ and preferred orientation index M < 0.1 (see Table V, Footnote b).^eThe outer layers were high-density, oriented PyC. The GA coating had an "onionring" laminar microstructure, whereas the IASL coating had a smooth microstructure. (See Table II for preparation and properties of these coatings.)^fII = 2300°C - 4 h + cooling + 2500°C - 30 min; III = 2300°C - 4 h + cooling + 2600°C - 30 min.^gDetermined by leaching the heated particles and the crucible in 8 N HNO₃ at 95°C for 8 h and analyzing the leach solution for uranium. Values are averages of duplicate samples heated separately at 2500 or 2600°C.^hThe densities of the GA inner pyrolytic carbons were:

	W-329I	W-331I	W-332I	W-330I
Before heating, g/cm ³	1.91-1.98	1.98	1.99	2.01
After 2300°C - 4 h, g/cm ³	1.92-2.05	2.07	2.07	2.11

ⁱThe outer layer for this batch was deposited in a carrier bed containing 3 g of the precoated particles and 30 g of 104- to 124- μ -diam carbon bed UC₂ particles, to establish the initial bed area at 1100 cm².

Fracture surfaces of the PyC coatings, prepared by breaking individual coated particles, were examined with a scanning electron microscope. The scanning electron micrographs (Fig. 4) show the delaminations that developed in many of the fragments when the particles were crushed and show the imprint on the inside of the PyC coating of the graphite shell on the core. However, the examination did not reveal significant microstructural differences between the two types of coatings.

Transmission electron microscope examination of two-stage carbon replicas of polished and etched sections of the two types of coatings, before and after heating, revealed what are believed to be the important differences between the two types of PyC. The electron micrographs are shown in Fig. 5. The as-deposited IASL PyC (on Batch GA-266-5, C-9 particles) etched poorly (1/2 h xenon plasma) but had a concentric layer structure with fine layers about 0.1 to 0.2 μ apart and coarse layers about 0.5 to 2 μ apart. After heat treatment at 2300°C for 4 h, the area be-

tween the coarse layers was smoother and the lamellae were etched deeper. After successive heating at 2300°C for 4 h, cooling, and heating at 2800°C for 30 min, many layers 0.1 to 1 μ apart, deeply etched and discontinuous, were observed (not shown). The as-deposited General Atomic PyC (on Batch GA-XEK-4444 particles) had layers 3 to 5 μ apart, with a poorly resolved sooty substance between the layers. After heat treatment at 2300°C for 4 h, the sooty material between lamellae appeared to be carbon black with projected diameters between 0.1 and 0.5 μ . After successive heating at 2300°C for 4 h, cooling, and heating at 2800°C for 30 min, the structure was similar to that obtained by 2300°C heating alone, except for the development of discontinuous lamellae about 1 μ apart (not shown).

The electron micrographs clearly show that the General Atomic PyC contained soot inclusions. These persisted and limited the bulk densification of the coating on heat treatment even though the preferred orientation increased with heat treatment at 2300°C

Heated 2300°C-4h, cooled,
and heated 2600°C-30 min

Heated 2300°C-4h, cooled,
and heated 2500°C-30 min

Batch GA-W-329

Batch GA-W-330

Microradiographs
100X

Microradiographs
100X

As
coated

Photomicrographs
Polarized light 500X

Fig. 3. Particles with two-layer coatings deposited by General Atomic in production-scale equipment.

Table VII

Results of Cyclic Heating of Coated Particles

Core Range, μ	Graphite Shell Thickness, μ	Coated Particle Batch No.	Inner Layer		Outer Layer		Total Act, μ			% U Exposed by Heat Treatment, %		
			Type	Act, μ	Type	Act, μ	a		b	10	15	20
104-147	2.0	CA-4424-4446	--	--	(a)	43	43	14	14	63	31	73
	2.0	CA-4424-36.00f	--	--	(a)	39	39	16	16	67	33	64
124-175	3.0	CA-4424-4426	--	--	(a)	49	49	5	5	30	12	43
	3.0	CA-442635, C-1 ^b	--	--	ISO ^c	50	50	0.3	0.3	5	2	11
124-175	3.0	CA-442635, C-6A ^b	ISO ^d	10	ISO	32	50	0.3	0.3	1.6	1	3.7
	3.1	CA-F-300125-S, C-1A ^b	ISO ^e	17	ISO	32	49	0.07	0.07	0.0	0.13	3
	3.2	CA-G-300125-S, C-1A ^b	ISO ^f	17	ISO	33	50	0.07	0.07	0.0	0.2	2.3
	4.2	CA-U-3291	(A)	15	(a)	35	50	2.4	2.4	20	5	43
	3.4	CA-U-3314	(A)	15	(a)	31	46	1.1	1.1	33	4	52
	3.1	CA-U-3321	(A)	17	(a)	29	46	1.0	1.0	23	4	62
	2.9	CA-F-300125-S, C-1A ^b	ISO ^g	12	ISO	20	40	0.03	0.03	2.6	0.2	7
104-147	2.7	CA-G-300125-S, C-1A ^b	ISO ^h	13	ISO	26	39	0.10	0.10	5	0.35	0
	3.5	CA-U-3301	(A)	9	(a)	26	35	5	5	37	11	47

^a Average value for 25 particles in a metallographic mount, normalized to the midplanes of the particles.

^b ACT = average coating thickness. The values do not include the graphite shells on the cores.

^c II = 2500°C - 4 h + cooling + 2500°C - 30 min.

III(3) = 2500°C - 4 h + cooling plus three cycles of 2500°C - 30 min + cooling.

III = 2500°C - 4 h + cooling + 2500°C - 30 min.

III(3) = 2500°C - 4 h + cooling plus three cycles of 2500°C - 30 min + cooling.

^d Determined by leaching the heated particles and the crucible in 0.5 MNa₂SO₄ at 95°C for 6 h and analyzing the leach solution for uranium. Values are averages of duplicate samples heated separately at 2500°C or 2550°C.

^e One-kg trial batch of particles coated by General Atomic. Production cores.

^f Eleven-kg crossblend of four nominal 3-kg batches coated by General Atomic. Production cores.

^g One-kg trial batch of particles coated by General Atomic. Experimental cores.

^h Coated by LASL. Experimental General Atomic cores.

ⁱ Two-kg batches of particles coated by General Atomic. Experimental cores.

^j HDI = LASL standard high-density, isotropic PyC. See Table V for preparation and properties.

^k IDO = LASL standard high-density, oriented PyC. See Table II for preparation and properties.

^l These General Atomic coatings varied from isotropic to somewhat oriented. See Footnote h of Table VI for densities.

^m The General Atomic PyC had an "onionring" lamellar microstructure. See Table II and Figs. 2 and 3.

CONFIDENTIAL

1000X

3000X

Batch GA-266-5,C-9 coated by IASL

Batch GA-XEK-4444 coated by General Atomic

Fig. 4. Scanning electron micrographs of fracture surfaces of pyrolytic-carbon particle coatings.

CONFIDENTIAL

CONFIDENTIAL

Before heating

Heated 2300°C - 4 h

Batch GA-266-5,C-9 coated by IASL

Batch GA-XEK-4444 coated by General Atomic

Fig. 5. Electron micrographs of two-stage carbon replicas of polished and etched surfaces of high-density, oriented pyrolytic-carbon particle coatings. 10,000X.

CONFIDENTIAL

CONFIDENTIAL

for 4 h as much as in the IASL PyC (see Table II). Presumably the persistent disordered regions in the General Atomic PyC provided paths for easy movement of melt through the coating and account for the inferior performance of particles with an outer layer of this type of PyC.

Extensive work has been done at IASL to modify and scale up fluidized-bed coating processes to avoid incorporation of soot into high-density, oriented PyC. That work will be described in a subsequent report.

4. SUMMARY

(1) Attempts were made to obtain kilogram quantities of improved coated particles for use in developmental Rover fuel elements. The particles were purchased from General Atomic on a fixed-price, best-efforts basis. Specifications called for the particles to contain General Atomic UC₂ cores with a complete graphite shell to be made like designated previous batches and to have PyC coatings with designated physical properties similar to those of coatings developed at IASL. Corresponding UC₂ cores were obtained with each batch of coated particles and were coated at IASL for comparison.

(2) The high-density, oriented PyC deposited in production equipment by General Atomic was an "onionring" variety of laminar coating. This PyC did not densify on pretreatment at 2300°C for 4 h as well as, and did not resist penetration by melt at 2500°C or higher temperatures as well as, the high-density, oriented PyC with a smooth microstructure deposited at IASL in 1-in.-diam equipment.

(3) Particles prepared by General Atomic with a nominal 40-μ-thick, single-layer coating of high-density, oriented PyC on 104- to 147-μ-diam production UC₂ cores or with a nominal 50-μ-thick, single-layer coating of that PyC on 124- to 175-μ-diam experimental UC₂ cores had substantially better thermal stability at 2500 or 2600°C for 30 min, following pretreatment at 2300°C for 4 h and cooling, than did standard General Atomic production particles. Twenty kg of particles of the first type were purchased and used to make developmental fuel elements for the Pewee-1 Reactor.

(4) Next, two concurrent improvements led to the hope that more stable coated particles could be obtained in kilogram quantities. These improvements were the preparation of substantially better experi-

mental UC₂ cores by General Atomic and the development at IASL of a very effective two-layer coating with an inner sacrificial layer of high-density, isotropic PyC and an outer resistant layer of high-density, oriented PyC. Four nominal 2.5-kg-U batches of particles with such cores and coatings were purchased from General Atomic in 1968. Again, the oriented PyC deposited as the outer layer in production equipment at General Atomic was the "onionring" variety of oriented laminar PyC. The particles were the most stable made by General Atomic to that date, but their performance fell short of that of the IASL-coated particles with the corresponding cores.

(5) Two-stage carbon replicas of polished and etched sections of the high-density, oriented pyrolytic carbons deposited in production equipment at General Atomic and in laboratory equipment at IASL were examined by transmission electron microscopy. The poorer performance of the General Atomic coating appeared to be due to incorporated soot that blocked densification of the coating during pretreatment of the particles and led to persistent disordered regions with poor resistance to penetration by melt.

ACKNOWLEDGMENTS

The authors thank I. L. Post, J. S. Boothe,* G. S. Mayne,* E. A. Asprey,* and R. E. Smith for assistance in various phases of this work. The authors also thank R. D. Baker for his continuing support and encouragement, L. L. Lyon for consultation and encouragement, members of the Analytical Chemistry Group for chemical analyses, C. G. Hoffman for crushing strength measurements, and T. G. Gregory, Jr., for scanning electron microscopy. The metallography was done by J. P. Bertino, the x-ray diffraction was done by J. A. O'Rourke, and the transmission electron microscopy was done by L. S. Levinson.

* IASL-New Mexico State University Undergraduate Cooperative Program.

CONFIDENTIAL

REFERENCES

1. R. J. Bard and A. W. Savage, Jr., "Development of Particles Coated with Pyrolytic Carbon," presented at the Thirteenth AEC Coated Particle Fuels Working Group Meeting, La Jolla, California, December 12-13, 1967 (Confidential).
2. R. J. Bard and H. R. Baxman, "Development of Particles Coated with Pyrolytic Carbon," presented at the Fourteenth AEC Coated Particle Fuels Working Group Meeting, Oak Ridge, Tennessee, November 20-21, 1968 (Confidential).
3. R. J. Bard, presented at the Fifteenth AEC Coated Particle Fuels Working Group Meeting, Los Alamos, New Mexico, December 10-11, 1969 (Confidential talk).
4. R. J. Bard, W. J. McCreary, A. W. Savage, Jr., H. R. Baxman, J. P. Bertino, S. W. Hayter, J. A. O'Rourke, and M. C. Tinkle, "Development of Particles Coated with Pyrolytic Carbon. I. Coatings from Methane at Low Temperatures," Los Alamos Scientific Laboratory Report LA-3496, January 1967 (Confidential).
5. R. J. Bard, W. J. McCreary, H. R. Baxman, J. P. Bertino, J. A. O'Rourke, S. W. Hayter, A. W. Savage, Jr., and M. C. Tinkle, "Development of Particles Coated with Pyrolytic Carbon. II. Coatings from Methane at High Temperatures," Los Alamos Scientific Laboratory Report LA-3601, March 1967 (Confidential).
6. R. J. Bard, H. R. Baxman, A. W. Savage, Jr., J. A. O'Rourke, W. J. McCreary, S. W. Hayter, J. P. Bertino, and M. C. Tinkle, "Development of Particles Coated with Pyrolytic Carbon. III. Coatings from Acetylene at Low Temperatures," Los Alamos Scientific Laboratory Report LA-3660, June 1967 (Confidential).
7. R. J. Bard, A. W. Savage, Jr., H. R. Baxman, W. J. McCreary, J. P. Bertino, S. W. Hayter, and J. A. O'Rourke, "Development of Particles Coated with Pyrolytic Carbon. IV. Coatings from Various Hydrocarbons at Low Temperatures," Los Alamos Scientific Laboratory Report LA-3767, February 1968 (Confidential).
8. R. J. Bard, H. R. Baxman, J. P. Bertino, and J. A. O'Rourke, "Pyrolytic Carbons Deposited in Fluidized Beds at 1200 to 1400°C from Various Hydrocarbons," Carbon 6, 603 (1968).
9. R. J. Bard, H. R. Baxman, J. A. O'Rourke, W. J. McCreary, A. W. Savage, Jr., and J. P. Bertino, "Development of Particles Coated with Pyrolytic Carbon. V. Doped Coatings," Los Alamos Scientific Laboratory Report LA-3984, November 1968 (Confidential).
10. R. J. Bard, L. L. Lyon, H. R. Baxman, J. P. Bertino, S. W. Hayter, and W. J. McCreary, "Development of Particles Coated with Pyrolytic Carbon. VI. Comparisons of Experimental UC₂ Cores," Los Alamos Scientific Laboratory Report LA-4139, May 1969 (Confidential).
11. R. J. Bard, H. R. Baxman, W. J. McCreary, S. W. Hayter, J. P. Bertino, J. A. O'Rourke, and A. W. Savage, Jr., "Development of Particles Coated with Pyrolytic Carbon. VII. Studies of Porous Carbon," Los Alamos Scientific Laboratory Report LA-4226, November 1969 (Confidential).
12. R. J. Bard, H. R. Baxman, J. P. Bertino, S. W. Hayter, J. A. O'Rourke, and W. J. McCreary, "Development of Particles Coated with Pyrolytic Carbon. VIII. Improved Core-Coat Combinations," Los Alamos Scientific Laboratory Report LA-4308, December 1969 (Confidential).
13. A. W. Savage, Jr., R. C. Feber, J. P. Bertino, H. R. Baxman, J. A. O'Rourke, and R. J. Bard, "Development of ZrC-Coated UC-ZrC Particles," Los Alamos Scientific Laboratory Report LA-4005, January 1969 (Confidential).
14. J. C. Bokros, "The Structure of Pyrolytic Carbon Deposited in a Fluidized Bed," Carbon 3, 17 (1965).
15. R. J. Bard, "Development of Pyrocarbon-Coated UC₂ Particles at LASL," presented at the Sixth AEC Coated Particle Fuels Working Group Meeting, Los Alamos, New Mexico, December 10-11, 1963 (Confidential).
16. J. C. Bokros and H. L. Sandefur, "Uranium Migration through Pyrolytic Carbons Deposited in a Fluidized Bed," General Atomic Report GA-5793, November 9, 1964 (Confidential).
17. R. J. Bard, "Development of Particles Coated with Pyrolytic Carbon," presented at the Eleventh AEC Coated Particle Fuels Working Group Meeting, Los Alamos, New Mexico, June 1-2, 1966 (Confidential).
18. J. C. Bokros, J. N. Graves, N. L. Sandefur, and A. S. Schwartz, "Uranium Migration through Carbon Coatings Deposited at High Temperatures in Fluidized Beds," General Atomic Report GA-7148, May 25, 1966 (Confidential).
19. L. L. Lyon, "Results of Pewee-1 Coated Particle Experiment," presented at the Fifteenth AEC Coated Particle Fuels Working Group Meeting, Los Alamos, New Mexico, December 10-11, 1969 (Confidential).
20. M. F. Browning, J. M. Blocher, Jr., V. M. Secrest, and A. C. Secrest, "Coating Fuel Particles with Pyrolytic Carbon," Battelle Memorial Institute Report BML-1643, August 16, 1963.

CONFIDENTIAL

APPENDIX A

SPECIFICATIONS FOR EXPERIMENTAL COATED PARTICLES (As distributed)

I. Specification CMB-8-4234 (March 7, 1967)

1. Preparation and Properties of 93%-Enriched

UC₂ Cores:

- 1.1 The cores shall be made using standard production conditions such as used by GA to make the cores in lots LY-113, LY-121, LY-124 and LY-125 of coated particles on IASL Purchase Order IA6-00050.
- 1.2 The cores shall have diameters of 104 to 147 microns (screened to minus 100 plus 150 Tyler mesh). The cores shall be 50 ± 5 wt % above and below 124 microns, i.e., 115 Tyler mesh.
- 1.3 The cores shall have at least 10.2 wt % carbon.
- 1.4 The cores shall contain no more than 3% non-spheres by count.

2. Preparation and Properties of Pyrolytic Carbon

Coatings and Coated Particles:

- 2.1 The pyrolytic carbon coatings shall be deposited from methane-diluent mixtures at temperatures not above 1350°C and not below 1200°C true fluidized bed temperature.
- 2.2 The coating thickness shall be 40 microns (minus 0 μ , plus 5 μ) including the graphite shell on the core, as determined by measurements on microradiographs.
- 2.3 The density of the as-deposited coating shall be in the range 2.00 to 2.12 g/cm³, with at least 2.08 g/cm³ desired.
- 2.4 The coating shall have a Bacon Anisotropy Factor of at least 12, as determined on deposits removed from graphite discs coated in fluidized beds of the particles delivered (Bokros technique). (See Batches 3383-119E and 3383-121E in Table VII of Report GA-7148.)
- 2.5 The exposed uranium, gas content and impurity content limitations of Specification CMB-8-3819 (as revised 3-25-64 and 5-3-65) shall apply to the lot of coated particles.

II. Specification CMB-8-4224 (Revised 2-26-67)

1. Preparation and Properties of 93%-Enriched

UC₂ Cores:

- 1.1 The cores shall be made using the feed composition and preparation temperature used by GA to make the UC₂ particles of Batch 1370 (300-g experimental batch) and Batch HI-3266ES

(3.8 kg production batch) on Purchase Order IA6-00050.

- 1.2 The cores shall have diameters of 124 to 175 microns (screened to minus 80 plus 115 Tyler mesh). The cores shall be 50 ± 5 wt % above and below 147 microns, i.e., 100 Tyler mesh.
- 1.3 The cores shall have 11.0 ± 0.2 wt % carbon.
- 1.4 The cores shall contain no more than 3% non-spheres by count.

2. Preparation and Properties of Pyrolytic Carbon Coatings and Coated Particles:

- 2.1 The pyrolytic carbon coatings shall be deposited from methane-diluent mixtures at temperatures not above 1350°C and not below 1200°C true fluidized bed temperature.
- 2.2 The coating thickness shall be 50 microns (minus 2 μ , plus 4 μ) including the graphite shell on the core, as determined by measurements on microradiographs.
- 2.3 The density of the as-deposited coating shall be in the range 2.00 to 2.12 g/cc, with at least 2.08 g/cc desired.
- 2.4 The coating shall have a Bacon Anisotropy Factor of at least 12, as determined on deposits removed from graphite discs coated in fluidized beds of the particles delivered (Bokros technique). (See Batches 3383-119E and 3383-121E in Table VII of Report GA-7148.)
- 2.5 The exposed uranium, gas content and impurity content limitations of Specification CMB-8-3819 (as revised 3-25-64 and 5-3-65) shall apply to the lot of coated particles.

III. Specification CMB-8-4234 (Revised 12-8-67)

1. Preparation and Properties of 93%-Enriched

UC₂ Cores:

- 1.1 The cores shall be made using standard production conditions such as used by GA to make the cores in lots LY-113, LY-121, LY-124 and LY-125 of coated particles on IASL Purchase Order IA6-00050.
- 1.2 The cores shall have diameters of 104 to 147 microns (screened to minus 100 plus 150 Tyler mesh). The cores shall be 50 ± 5 wt % above and below 124 microns, i.e., 115 Tyler mesh.
- 1.3 The cores shall have at least 10.2 wt % carbon.
- 1.4 The cores shall contain no more than 3% non-spheres by count.

CONFIDENTIAL

CONFIDENTIAL

2. Preparation and Properties of Pyrolytic Carbon Coatings and Coated Particles:

- 2.1 The pyrolytic carbon coatings shall be deposited from methane-diluent mixtures at temperatures not above 1350°C and not below 1200°C true fluidized bed temperature.
- 2.2 The coating thickness shall be 40 microns (minus 0 μ , plus 5 μ) including the graphite shell on the core, as determined by measurements on microradiographs.
- 2.3 The density of the as-deposited coating shall be in the range 2.00 to 2.12 g/cc, with at least 2.08 g/cc desired.
- 2.4 The coating shall be the oriented laminar type and the preferred orientation shall be determined on deposits removed from graphite discs coated in the fluidized beds of particles (Bokros technique). The particles will be acceptable with regard to Bacon Anisotropy Factor (BAF) if the following conditions are met:
 - 2.4.1 The discs used to determine the character of the coating on the particles shall appear to have the same structure and coating thickness as that observed in samples of the coated particles using a metallographic method and observed at 500X.
 - 2.4.2 The results of the plot of intensity versus angle curve shall be such that at 19 degrees the relative intensity shall be less than 50%.*
- 2.5 The exposed uranium, gas content and impurity content limitations of Specification CMB-8-3819 (as revised 3-25-64 and 5-3-65) shall apply to the lot of coated particles.

IV. Specification CMB-8-4335 (March 25, 1968)

1. Preparation and Properties of 93%-Enriched UC₂ Cores:

- 1.1 The cores shall be made using the same conditions that were used to prepare Batch 4420ES cores on LASL Purchase Order LA7-41717.
- 1.2 The cores shall have diameters of 124 to 175 microns (screened to minus 80 plus 115 Tyler mesh). The cores shall be 50 $\pm$ 5 wt % above

and below 147 microns, i.e., 100 Tyler mesh.

1.3 The cores shall have 11.0 $\pm$ 0.2 wt % carbon.

1.4 The cores shall contain no more than 3% non-spheres by count.

2. Preparation and Properties of Pyrolytic Carbon Coatings and Coated Particles:

2.1 The coated particles shall have two-layer pyrolytic carbon coatings.

- 2.1.1 The inner layer of pyrolytic carbon shall meet the following requirements:
 - (a) It shall be deposited at temperatures not above 1400°C and not below 1200°C true fluidized bed temperature.
 - (b) It shall have a thickness of 20 microns (minus 2 μ , plus 2 μ) including the graphite shell on the core, as determined by measurements on microradiographs.
 - (c) Its density in the as-deposited condition shall be in the range 1.90 to 1.95 g/cc.
 - (d) It shall be the type commonly known as "low temperature isotropic (LTI)" with a Bacon Anisotropy Factor (BAF) not more than 1.15 and with a microstructure that shows no appreciable optical activity under polarized light.
- 2.1.2 The outer layer of pyrolytic carbon shall meet the following requirements:
 - (a) It shall be deposited from methane-diluent mixtures at temperatures not above 1350°C and not below 1200°C true fluidized bed temperature.
 - (b) It shall have a thickness of about 30 microns, such that the total thickness of the two-layer coating is 50 microns (minus 0 μ , plus 4 μ) including the graphite shell on the core, as determined by measurements on microradiographs.
 - (c) Its density in the as-deposited condition shall be in the range 2.00 to 2.12 g/cc, with at least 2.08 g/cc desired.
 - (d) It shall be the oriented laminar type and the preferred orientation shall be determined on deposits removed from graphite discs coated in the fluidized beds of particles (Bokros technique). The particles will be acceptable with regard to Bacon Anisotropy Factor (BAF) if the following conditions are met:

* See Appendix B.

CONFIDENTIAL

CONFIDENTIAL

- (1) The discs used to determine the character of the coating on the particles shall appear to have the same structure and coating thickness as that observed in samples of the coated particles using a metallographic method and observed at 500X.

- (2) The results of the plot of intensity versus angle curve shall be such that at 19 degrees the relative intensity shall be less than 50%.

2.2 The exposed uranium, gas content and impurity content limitations of Specification CMB-8-3819 (as revised 3-25-64 and 5-3-65) shall apply to the lot of coated particles.

V. Specification CMB-8-4363 (June 20, 1968)

1. Preparation and Properties of 93%-Enriched UC_2 Cores:

- 1.1 The cores shall be made using the same conditions that were used to prepare Batches 4420ES and F-300LES cores on LASL Purchase Order LA7-41717.
- 1.2 The cores shall have diameters of 104 to 147 microns (screened to minus 100 plus 150 Tyler mesh). The cores shall be 50 ± 5 wt % above and below 124 microns, i.e., 115 Tyler mesh.
- 1.3 The cores shall have 11.0 ± 0.2 wt % carbon.
- 1.4 The cores shall contain no more than 3% non-spheres by count.

2. Preparation and Properties of Pyrolytic Carbon Coatings and Coated Particles:

- 2.1 The coated particles shall have two-layer pyrolytic carbon coatings.
 - 2.1.1 The inner layer of pyrolytic carbon shall meet the following requirements:
 - (a) It shall be deposited at a temperature not to exceed 1400°C.
 - (b) It shall have a thickness of 14 microns (minus 2 μ , plus 2 μ) including the graphite shell on the core, as determined by measurements on microradiographs.
 - (c) Its density in the as-deposited condition shall be in the range 1.90 to 1.95 g/cc.
 - (d) It shall be the type commonly known as "low temperature isotropic (LTI)" with a Bacon Anisotropy Factor (BAF) not more than 1.15 and with a microstructure that shows no appreciable optical activity

under polarized light.

- 2.1.2 The outer layer of pyrolytic carbon shall meet the following requirements:

- (a) It shall be deposited from methane-diluent mixtures at temperatures not above 1350°C and not below 1150°C true fluidized bed temperature.
- (b) It shall have a thickness of about 28 microns, such that the total thickness of the two-layer coating is 42 microns (minus 2 μ , plus 2 μ) including the graphite shell on the core, as determined by measurements on microradiographs.
- (c) Its density in the as-deposited condition shall be in the range 2.00 to 2.12 g/cc, with at least 2.08 g/cc desired.
- (d) It shall be the oriented laminar type and the preferred orientation shall be determined on deposits removed from graphite discs coated in the fluidized beds of particles (Bokros technique). The particles will be acceptable with regard to Bacon Anisotropy Factor (BAF) if the following conditions are met:

- (1) The discs used to determine the character of the coating on the particles shall appear to have the same structure and coating thickness as that observed in samples of the coated particles using a metallographic method and observed at 500X.
- (2) The results of the plot of intensity versus angle curve shall be such that at 19 degrees the relative intensity shall be less than 50%.

2.2 The exposed uranium, gas content and impurity content limitations of Specification CMB-8-3819 (as revised 3-25-64 and 5-3-65) shall apply to the lot of coated particles.

REF ID: A66666
CONFIDENTIAL

APPENDIX B

DETERMINATION OF PREFERRED ORIENTATIONS OF PYROLYTIC CARBONS AT LASL AND GENERAL ATOMIC

The preferred orientation index M is given by $I(\theta) = \cos^M \theta$, where $I(\theta)$ is the relative x-ray diffraction intensity at angle θ to the normal of the surface. The Bacon anisotropy factor is given by

$$\text{BAF} = \frac{2 \int_0^{\pi/2} I(\theta) \cos^2 \theta \sin \theta \, d\theta}{\int_0^{\pi/2} I(\theta) \sin^3 \theta \, d\theta}.$$

When $\cos^M \theta$ is substituted for $I(\theta)$, the right side of this expression reduces to $M + 1$.

The value of M was determined at LASL from corrected x-ray diffraction data out to about $\theta = 40^\circ$ from data obtained by a reflection diffractometer technique. When the relative intensity went to background at $\theta \leq 50^\circ$, BAF was calculated at LASL assuming that there were no contributions at higher angles (see Table II). LASL correlations between preferred orientation and resistance of pyrolytic carbon to migration were thus based on the shape of the relative intensity vs angle curve at $\theta \leq 50^\circ$.

General Atomic obtained its x-ray diffraction data by a transmission method using film recording of intensities out to $\theta = 90^\circ$. The General Atomic calculations of BAF thus included any contributions at high angles, which entered the calculation strongly and lowered the calculated BAF. LASL calculations applied to General Atomic intensity data indicated suitably high preferred orientation in many cases where General Atomic calculations of BAF did not.

The relative intensity at $\theta = 19^\circ$ was chosen as a convenient method of reporting preferred orientations. The requirement that $I(\theta)$ be less than 50% at $\theta = 19^\circ$ corresponds to the requirement of $M \geq 12.4$.

Alt/bw:142

CONFIDENTIAL