~~CONFIDENTIAL~~
~~RESTRICTED DATA~~
Atomic Energy Act 1954

RECORD COPY

SNPO-C

Astronuclear

Bease
Thurke

WANL-TME-1022

October 30, 1964

MASTER

Westinghouse Astronuclear Laboratory
Contribution to the
Eighth Meeting of the Particle Fuels Working Group

November 17 and 18, 1964

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, 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.

EVALUATION OF FUEL PARTICLE:

Prepared by:

A. Boltax, W. Brizes, A. Feild, and D. Jacobs

**SPECIAL REVIEW
FINAL
DETERMINATION**
Class: U

Reviewed by JRP
Class. U 5-4-82

Classification cancelled (or changed to) _____
by authority of DEC
by H.F.C. TIC, date SEP 10 1973

RECORD COPY

INFORMATION CATEGORY
Confidential - Restricted Data

A. Boltax 10/30/64
Authorized Classifier Date

Group 1 - Excluded from Automatic
Downgrading and Declassification

(The preliminary information presented in this report should not be published without prior written approval of the Westinghouse Astronuclear Laboratory. The work performed was supported by the Space Nuclear Propulsion Office.)

~~CONFIDENTIAL~~
~~RESTRICTED DATA~~
Atomic Energy Act 1954

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Evaluation of Vendor Coated Particles (A. L. Feild)

Work has continued on the evaluation of qualification, production, and development type coated particles from participating vendors. Thermal migration testing has been conducted at 2300°C for four hours on all preproduction qualification and production lot samples. The development of a quantitative thermal migration test, based on micro-radiographic techniques, was described in detail at the last Particle Fuels Working Group meeting. The results of this standard migration test on recent sample lots are shown in Table I.

These data indicate that the quality of fuel beads has continued to be excellent on production lot samples of both General Atomic and Carbon Products fuels. The 2300°C-4 hr. test requirement was met adequately and the minimum coating thickness after test was from 2-6 microns less than the 18-25 micron coating thickness before test. The percentage of particles completely migrated after this test was generally within the 3 per cent maximum set forth in WANL Specification 30050-B. The $X - 1.6\sigma$ was considerably greater than the 5 micron minimum required for acceptance and normally exceeded 10 microns.

One development sample of 3M material exhibited excellent performance at 2300°C for four hours, although the average coating thickness of 13 microns after test was somewhat less than the normal thickness expected.

In anticipation of future requirements for higher fuel operating temperatures, some work was done in testing thermal migration characteristics at 2500°C and 2600°C for exposures of 1/2 hour. These results are shown in Table II. It may be noted that the UC_2 core is molten at temperatures above approximately 2450°C, and the liquid can take a certain amount of carbon into solution. This means that the integrity of the coating is much more difficult to maintain than would be expected from the increased diffusion rate of uranium solely due to the higher temperature. The data show that none of the samples, all of which passed the 2300°C - 4 hour test, were able to survive either 2500°C or 2600°C for 1/2 hour with low percentages of total migration.

Table I
Thermal Migration Tests - Current Materials

Sample ⁽¹⁾	Test Condition	Avg. Coating Thick. (μ)	$\bar{X} - 1.6\sigma^{(2)}$	Minimum Coating Thick. (μ)	% Particles Migrated
GA 44001	As-received	22.1	18.9	20.8	0
		19.1	17.2	17.8	0.3
GA 44002	As-received	20.7	16.9	18.3	0
		21.5	17.8	--	--
GA 44003	As-received	18.3	14.8	16.4	0
		19.6	16.1	--	--
GA 44001	2300°C - 4 hrs.	16.5	10.3	13.0	6.8
		17.5	13.3	14.4	2.8
GA 44002	2300°C - 4 hrs.	15.2	8.3	12.9	3.2
		17.2	12.2	14.4	3.2
GA 44003	2300°C - 4 hrs.	18.6	15.1	14.9	0.9
		19.3	14.8	16.3	0.9
		19.3	16.3	17.4	0.9
GA 44004	2300°C - 4 hrs.	21.5	15.5	19.3	0.7
		20.9	15.7	17.8	0.7
UC 43001	As-received	24.4	14.9	21.8	1.0
		23.3	15.6	20.1	1.2
UC 43002	As-received	21.7	11.3	15.9	2.4
		22.5	12.7	--	--
UC 43001	2300°C - 4 hrs.	17.4	8.8	12.7	3.8
		18.2	10.5	14.1	2.3
		20.8	11.2	17.9	2.6
		18.4	9.3	13.9	2.8
UC 43002	2300°C - 4 hrs.	16.2	6.1	12.3	0.36
		17.5	6.3	14.0	0.36

(1) GA -- General Atomic
 UC -- Union Carbide (Carbon Products)
 Dav -- Davison

(2) $\bar{X} - 1.6\sigma \geq 5\mu$ for acceptance

Table I (continued)

<u>Sample⁽¹⁾</u>	<u>Test Condition</u>	<u>Avg. Coating Thick. (μ)</u>	<u>$\bar{X} - 1.6\sigma^{(2)}$</u>	<u>Minimum Coating Thick. (μ)</u>	<u>% Particles Migrated</u>
UC 43003	2300°C - 4 hrs.	16.9	7.5	14.4	1.4
UC 43004	2300°C - 4 hrs.	16.1	5.9	13.4	1.4
3M	2300°C - 4 hrs.	13.0	9.0	11.5	0.3
		13.1	10.2	11.7	0
		12.3	9.5	10.8	0.3

Table II
Thermal Migration Tests at Temperature Above 2300°C

<u>Sample</u>	<u>Test Condition</u>	<u>Minimum Coating Thick. (μ)</u>	<u>% Particles Migrated</u>
GA 44002	2500°C - 1/2 hr.	5.6	44.0
GA 44003	2500°C - 1/2 hr.	6.9	52.0
UC 43002	2500°C - 1/2 hr.	--	100.0
UC 43001	2600°C - 1/2 hr.	--	100.0
LASL 588	2500°C - 1/2 hr.	--	83.0
UC D 49A	2500°C - 1/2 hr.	--	80.0
	2600°C - 1/2 hr.	--	100.0
UC D 54A	2600°C - 1/2 hr.	--	100.0
Y-12 Li 111	2600°C - 1/2 hr.	--	100.0

Another important aspect of fuel particle behavior is the effect of thermal cycling on the coating integrity. Reactor restart will introduce a thermal cycling effect which might be of considerable importance relative to fuel lifetime and performance. To simulate such a condition, thermal cycling of two coated particle samples was performed in the following manner:

Heat up to 2300°C	15 min.	
Hold at 2300°C	30 min.	Repeat 7 times
Cool down to black heat	15 min.	

The results of this treatment are shown in Table III. Both the Union Carbide and General Atomic particles behaved satisfactorily in this test. The average coating thickness of the two materials after the first cycle were within one micron of each other. After the seventh cycle, they remained essentially the same as at the start. The GA material showed a greater total of completely migrated particles than the UC material. The latter fuel showed practically no migration during any of the individual cycles.

The above cycling tests are preliminary. There is an anomaly in the reported values of particles totally migrated due to variations in behavior of individual particles in progressive samples. However, it appears that particles currently available in production quantities will be able to survive a large number of thermal cycles without appreciable deterioration.

Mechanical Damage Studies (W. Brizes)

During the fabrication of NERVA fuel elements, the elements are leached in HCl to remove some of the exposed UC_2 before the NbC vapor coating step. Leach losses vary, but range from 7 to 14% of the uranium in the extruded elements. The major portion of the loss (a calculated maximum of 6.1%) is thought to be from particles whose PyC coating was cut during the machining of the graphitized elements to final dimensions. It is postulated that the excess loss is from fuel particles whose PyC coatings are damaged during fabrication prior to leaching and the UC_2 , below the exposed surface, is subsequently leached.

Table III
Thermal Cycling Tests - Development Samples

<u>Sample</u>	<u>Test Condition</u>	<u>Avg. Coating Thick. (μ)</u>	<u>X - 1.6σ</u>	<u>Min. Coating Thick. (μ)</u>	<u>% Particles Migrated</u>
UC D 54A	2300°C 7 cycles at 1/2 hr. each	18.7	13.6	15.8	1.4
		19.1	14.7	16.1	0
		19.2	13.4	16.8	0.6
		19.6	15.8	17.0	0.6
		20.2	14.7	17.6	0
		19.5	14.7	18.0	0
		20.9	16.3	17.3	0
GA EK 43	2300°C 7 cycles at 1/2 hr. each	19.6	6.2	12.9	0.5
		19.2	12.8	15.3	0.7
		20.4	9.5	18.1	2.0
		19.3	12.3	15.6	1.1
		18.6	9.0	14.6	4.8
		19.2	11.4	16.3	4.9
		19.9	9.2	16.8	1.1

To determine whether damage is occurring during the first stages of fabrication, i.e., the mixing, grinding or extrusion processes, samples of fuel mixes (particles, varcum, lampblack, flour), were taken from each of the above mentioned processes and leached to remove all of the exposed uranium. Two types of leaching media were used, chlorine gas at 1000°C and a 50/50 nitric acid solution at 90°C. Both methods appeared equally effective in leaching out the exposed uranium. Also, both methods indicated that as fabrication proceeded fuel particle damage increased up to a maximum of 0.4 per cent. The leaching results are given in Table IV for the final extrusions only since they contain the cumulative damage of all prior processes.

The maximum of 0.4 per cent uranium leachable will certainly not account for the uranium lost in the fuel element leaching process. Thus, if damage is occurring to the particles below the exposed surface, it must be between the final extrusion and the leaching processes, i.e., one of the heat treatments (cure, bake, or graphitization) and, or, the machining of the element to final dimensions. Work is presently being directed to determine if damage is actually occurring during one of these later processes.

Pyrocarbon Deposition in Fluidized Beds (E. Fatzer and M. Monkelis)

Examination of various data reported on pyrocarbon coating of UC_2 particles in fluidized beds revealed that a log-log plot of the rate of thickness increase (microns/hour) versus methane concentration produced a family of straight lines with essentially equivalent slopes (see Figure 1). The displacement of individual lines was ascribed to differences in deposition temperature, experimental equipment, and other operating parameters. Table V summarizes the available data reported on operating parameters. Figure 1 also shows results of WANL pyrocarbon deposition experiments. Duplex coated particles produced in this study demonstrate excellent migration resistance after four hours at 2300°C.

Reflection Electron Microscope Studies (W. Brizes)

The reflection method of electron microscopy which has been applied to fuel studies at Hanford Laboratories, has been used to observe the surface topography of sectioned

Figure 1 - Deposition Rate vs. Volume Fraction of Methane
 for Pyrocarbon Coating of UC₂ Particles

Table IV
Uranium Leachable from Damaged Particles Separated from
As-extruded Elements

<u>Sample</u>	<u>Application</u>	<u>% U Leachable by Chlorine at 1000°C for 3 hrs.</u>	<u>% U Leachable by 1 N HNO₃ at 90°C for 4 hrs.</u>
GA pre-production batch	NRX A-3 NRX A-4	0.392*	
CP pre-production batch	NRX A-3 NRX A-4	0.395	
NUMEC Batch 1119	NRX A-2		0.220
NUMEC Batch 1111	NRX A-2		0.324
NUMEC Batch 1115	NRX A-2		0.266
NUMEC Batch 1112 Batch 1253	NRX A-2		0.072 and 0.047 (2nd analysis)
Davison No. 25019			0.128 and 0.145 (2nd analysis)
3M No. 12017			0.164 and 0.169 (2nd analysis)

* As-received particles showed 0.0081 per cent leachable uranium. Heat treatment for four hours at 2300°C increased the leachable uranium to 0.280 per cent.

~~CONFIDENTIAL~~
~~RESTRICTED DATA~~

Table V
Operating Parameters for Fluidized Bed
Pyrocarbon Coating of UC_2 Particles

Laboratory	Reactor Diameter (in.)	Inlet Diameter (in.)	Charge Weight (gms)	Reactant Gas	Total Gas Flow Rate (l/min.)
LASL ⁽¹⁾	1/2	3/32-3/8	25	CH ₄	2.63
ORNL ⁽²⁾	3/4		10	CH ₄	0.76
Batelle ⁽³⁾ Geneva	--		--	CH ₄	2.67
R. A. E. ⁽⁴⁾ Farnborough	1		--	CH ₄	2.0
WANL	5/8	3/32	10	CH ₄	2.67

- (1) CMB-8-3842 Development of Pyrocarbon-Coated UC_2 Particles Compiled by R. J. Bard (Presented at 7th Particle Meeting, May 1964).
- (2) ORNL 64-5-17 Coated Particle Fuel Activity Letter for Period November 15, 1963, to May 15, 1964 - Part I (Presented at 7th Particle Meeting, May 1964).
- (3) TID-7654
pp 462-467 Carbon Coated Particles for Dispersion Fuels by A. Auriol and C. David, BML, Geneva
G. Kurka and E. LeBoulbin, C. E. A., Department de Metallurgie, Grenoble.
- (4) TID-7654
pp. 358-369 Coated Particle Fuel for the Dragon Reactor Experiment by R. A. U. Huddle, J. R. Gough, and H. Beutler - O.E.C.D. High Temperature Reactor Project - Dragon Project Office, A. E. E., Winfrith.

~~CONFIDENTIAL~~
~~RESTRICTED DATA~~
~~Atomic Energy, AEC-1178~~

and polished PyC coated UC_2 fuel particles in a graphite matrix by a reflected electron beam. The beam makes a low angle of incidence and reflection ($<30^\circ$) with the sample and then strikes the photographic plate at right angles. Thus, when looking at the photomicrographs, one sees the coated particle at a shallow angle relative to the surface of the sample and the circular coated particle appears elliptical.

Electron photomicrographs of two migrated fuel particles are shown in Figures 2 and 3 with corresponding photomicrographs made with an optical microscope. It is clear that the topography of the coated particles becomes apparent when viewed by this technique. In Figure 2 for example; 1) the graphite matrix is well bonded to the pyrocarbon coating, 2) there is an apparent difference in height across the delamination, 3) the migration zone appears rough, 4) the UC_2 core is raised due to differences in hardness of the carbide and pyrocarbon in polishing, thus casting a shadow into the foreground, 5) the lines on the UC_2 core are probably ppt's of UC, and 6) the surface is contaminated with polishing debris.

High temperature studies can be made with this technique since the actual sample is used, not a replica. Temperatures approaching $2700^\circ C$ have been achieved at the Hanford Laboratory with a modification of the JEM 6A microscope used here; and thus, it seems probable that migrating coated particles can be observed at high temperature with the use of electron reflection techniques.

Steady-state Irradiation of NERVA Fuel Material (D. Jacobs and C. Glassmire)

Introduction

This work is a continuation of the work reported at the last meeting. The earlier results were based on metallographic examination of three fuel pellets. Sixteen NERVA fuel samples have now been evaluated, and the results are compiled below.

Evaluation of Results

A total of sixteen NERVA fuel samples have been irradiated. Each sample received one of the following pre-irradiation treatments:

1. Heated in vacuum to $2400^\circ C$ for 0.5 hour then held at $100^\circ C$ in 100% relative humidity for 24 hours.

600X Optical Microscope

3500X Electron Reflection Microscope (JEM GA)
at Room Temperature

Figure 2 - Photomicrographs of a Coated UC_2 Particle from
Element 9-11269, 51 inches As-graphitized

- 12 -

600X Optical Microscope

3500X Electron Reflection Microscope (JEM GA)
at Room Temperature

Figure 3 - Photomicrographs of a Coated UC_2 Particle from
Element 9-11269, 51 inches As-graphitized

2. Machined from a NERVA fuel element which had been subjected to a 2.75 minute hydrogen corrosion test at 2500°C (surface temperature).

3. No pre-irradiation treatment.

The test conditions and results are summarized in Tables VI, VII, and VIII. The untreated NERVA fuel material exhibited excellent stability during the irradiation. All untreated samples retained their structural integrity and suffered no dimensional changes. Temperatures and irradiation times are given in the tables.

The irradiated, hydrogen-corroded and hydrolized materials suffered considerable damage. All samples became friable and were severely cracked. Those hydrogen corroded samples which remained intact suffered significant dimensional changes ($\geq 4\%$). Cracking was also observed in those unirradiated hydrogen corroded and hydrolized samples which were subjected to the longer heat treatment (≥ 130 minutes). However, this cracking was considerably less severe than that observed in the irradiated samples.

The crack patterns which developed in the irradiated hydrogen corroded samples were indicative of radial and tangential stresses. It is believed that these stresses were the results of (a) thermal gradients and (b) the residual stresses inherent to the anisotropic fuel material.

During the irradiation the largest contribution to the developed stresses was undoubtedly made by the thermal gradient. However, thermal gradients were essentially absent during heat treatment and the stresses developed within the control samples were derived primarily from residual stresses.

In light of the above and considering the experimental results it is clear that hydrogen corrosion and UC_2 hydrolysis both serve to degrade the mechanical strength of NERVA fuel. The effects of hydrogen attack are readily explained by conventional corrosion theory, i. e., a general loss and degradation of matrix material. However, the effect of UC_2 hydrolysis is not so clearly understood. Preliminary studies indicate that a hydrolysis treatment, similar to that received by the irradiation samples, reduces the room temperature, compressive strength of NERVA fuel material by approximately 30%.

Table VI
Test Results - As-Received Fuel Material

Pellet	Mean Temp., °C		Exposure Time (min.)	Burn-up ³ (fiss/cm ³) x 10 ¹⁷	Results
	Center	Surface			
3M	2420	2125	25.2	0.334	Pellet intact and exhibited good structural integrity. No dimensional changes. No significant UC ₂ migration.
3M-B*	2250	2250	25.2	---	Same as 3M
4M	2255	1990	100.2	1.22	Same as 3M
4M-B*	2220	2220	100.2	---	Same as 3M
6M-B*	1980	1980	270.0	---	Same as 3M
5M-B*	1860	1860	130.8	---	Same as 3M
5M	1580	1420	130.8	0.964	Same as 3M
6M	1380	1240	270.0	1.65	Same as 3M
9-1**	3050	2650	76.5	1.36	Pellet intact and exhibited good structural integrity. No dimensional changes. Metallography not completed.
9-2**	2900	2530	76.5	1.22	Same as 9-1
9-3**	2730	2400	76.5	1.10	Same as 9-1
9-4**	2560	2780	76.5	0.98	Same as 9-1

* Unirradiated controls

** Data are preliminary.

Table VII
Test Results - Pellets Machined from an Element which
Failed the Hydrogen Corrosion Test

Pellet	Mean Temp., °C		Exposure Time (min.)	Burn-up ₃ (fiss/gm) × 10 ³	Results
	Center	Surface			
3T	2240	1970	25.2	0.299	Pellet was intact but covered with a network of cracks. Increase in diam: 4.3 %.
4T	2140	1890	100.2	1.13	General description same as 3T. Pellet extremely friable and broke during normal handling. Increase in diam: 4 %.
3T-B*	2080	2080	25.2	---	Pellet retained structural integrity.
4T-B*	2040	2040	100.2	---	Pellet retained structural integrity.
6T-B*	1740	1740	270.0	---	Pellet intact but fine cracks present.
5T-B*	1700	1700	130.8	---	Pellet intact but fine cracks present.
5T	1500	1360	130.8	0.883	Same as 4T
6T	1240	1120	270.0	1.44	Same as 3T. Increase in diam: 4.3 %. Increase in height: 3.4 %.

* Unirradiated control pellets.

Table VIII
Test Results - Fuel Material with Hydrolyzed UC₂

Pellet	Wt. Gain (%)	Mean Temp., °C		Time (min.)	Burn-up (fiss/cm ³) x 10 ⁻¹⁷	Results
		Center	Surface			
3B	0.235	2555	2250	25.2	0.375	Pellet friable. Broken while still in capsule. Sample covered with network of cracks.
3B-B*	0.276	2420	2420	25.2	---	Good structural integrity.
4B-B*	0.238	2400	2400	100.2	---	Good structural integrity.
4B		2375	2100	100.2	1.31	Same as 3B
6B-B*	0.307	2020	2020	270.0	---	Sample intact but some fine cracks present.
5B-B*	0.316	2020	2020	130.8	---	Same as 6B-B
5B	0.224	1760	1580	130.8	1.11	Same as 3B
6B	0.204	1520	1380	270.0	1.88	Pellet broken into extremely small pieces (almost a powder)

* Unirradiated control pellets.

CONFIDENTIAL
RESTRICTED DATA
Atomic Energy

Neglecting the water of hydration, the molar volume of UO_2 is 6.63% greater than that of UC_2 . Consequently, if the UC_2 and graphite matrix are in intimate contact, hydrolysis would result in the formation of high local stresses. These would contribute locally to the residual stresses thereby inducing microcracking and/or serving to reduce the apparent strength of the fuel material.

CONFIDENTIAL
RESTRICTED DATA
Atomic Energy