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WESTINGHOUSE ASTRONUCLEAR LABORATORY

CONTRIBUTION TO THE

NINTH MEETING OF THE PARTICLE FUELS WORKING GROUP

May 25-27, 1965

MASTER

EVALUATION OF FUEL PARTICLES

Unclassified

Prepared by:

A. L. Feild, Jr. and W. F. Brizes

SPECIAL REVIEW FINAL DETERMINATION	Reviewers	Class.	Date
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EVALUATION OF VENDOR COATED PARTICLES (A. L. Feild, Jr.)

The evaluation of qualification, production, and development type coated particles from participating vendors has continued on a routine basis during the past six month period. Thermal migration testing has been conducted at 2300°C-4 hr. on all preproduction qualification and production lot samples, according to WANL-PDS-30050-B. Microradiographic evaluation of as-coated and heat treated particles of all lots examined during this period are summarized in Table I.

An examination of Table I reveals General Atomic and Union Carbide (Carbon Products) material to be the only production types tested. A substantially greater number of lot samples of the UC material were tested. The GA samples passed the total migration test and the $\bar{X}-1.6\sigma$ minimum in all lots tested. Although $\bar{X}-1.6\sigma > 5\mu$ is called for in the specification, the GA material never dropped below 14.8μ and ranged from $14.8-22.4\mu$, with average coating thicknesses from $18.6-26.8\mu$. Total migration, limited by specification to 3% of the total of particles counted, generally was less than 1%, with no lots exceeding 2.5%. The Union Carbide particle lots exhibited mixed behavior, some being exceptionally good, and some failing to pass the required specifications. The causes for poor performance in some of the lots have been determined and more recent lots evaluated have demonstrated consistent acceptability. On the basis of Table I data, 10 lots out of 28 tested failed the 3% maximum total migration specification. The remaining lots exhibited total migration behavior from 0-3%, with the average approximately 1.8%. Average

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TABLE I

Thermal Migration Tests - Current Materials

Sample*	Test Condition	$\bar{X}$ = Avg. Coating Thickness	$\bar{X}-1.6\sigma^{**}$	Min. Coating Thickness	% Particles Migrated
		(μ)	(μ)	(μ)	
GA 44003	2300°C-4 hr.	18.6	15.1	14.9	0.9
GA 44003	2300°C-4 hr.	19.3	14.8	16.3	0.9
GA 44003	2300°C-4 hr.	19.3	16.3	17.4	0.4
GA 44004	2300°C-4 hr.	21.5	15.5	19.3	0.7
GA 44004	2300°C-4 hr.	21.7	17.9	18.4	0
GA 44005	2300°C-4 hr.	20.9	15.7	17.8	0.2
GA 44006	As-received	24.5	20.1	21.8	0.2
GA 44006	2300°C-4 hr.	21.6	15.2	18.4	0.8
GA 44007	2300°C-4 hr.	25.3	20.8	23.1	0.3
GA 44008	As-received	23.2	19.6	20.5	0
GA 44008	2300°C-4 hr.	25.0	19.5	23.3	0.6
GA 44009	As-received	23.9	20.2	20.6	0.2
GA 44009	2300°C-4 hr.	26.8	20.2	23.2	2.6
GA 44010	As-received	23.8	20.7	21.0	0
GA 44010	2300°C-4 hr.	26.5	22.4	24.0	0
GA 44011	2300°C-4 hr.	26.5	22.1	23.5	0.4
GA 44012	2300°C-4 hr.	26.6	19.1	22.5	0.9
GA 44013	2300°C-4 hr.	22.2	16.7	18.6	0.5
GA 44014	2300°C-4 hr.	20.9	16.1	18.3	0.4
GA 44015	2300°C-4 hr.	20.4	16.4	17.6	0.2
GA 44016	2300°C-4 hr.	20.5	16.4	17.1	0.2
GA 44017	2300°C-4 hr.	20.8	15.9	16.6	1.5
GA 44018	2300°C-4 hr.	20.4	15.0	16.9	0.8
GA 44019	As-received	23.2	17.5	19.3	0.3
GA 44019	2300°C-4 hr.	19.4	14.9	16.7	0.6
GA 44019	2300°C-4 hr.	21.7	16.8	18.0	0
GA 44020	2300°C-4 hr.	20.0	13.3	16.1	0.4
GA 44020	2300°C-4 hr.	22.1	17.4	17.7	0.7
GA 44021	2300°C-4 hr.	20.5	17.6	17.4	0
GA 44022	2300°C-4 hr.	20.9	17.5	17.7	0.3
GA 44023	2300°C-4 hr.	22.1	17.3	18.3	0.3
GA 44024	As-received	22.8	19.5	20.0	0
GA 44025	As-received	23.0	19.6	19.6	0
GA 44026	2300°C-4 hr.	21.9	18.3	18.2	0
GA 44029	2300°C-4 hr.	20.2	15.7	16.6	0.7

* GA - General Atomic

UC - Union Carbide (Carbon Products)

** $\bar{X}-1.6\sigma \geq 5$ for acceptance

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Table I Cont'd.

Sample*	Test Condition	$\bar{X}$ = Avg. Coating Thickness		Min. Coating Thickness	% Particles Migrated
		$\bar{X} - 1.6\sigma^{**}$	$\bar{X} + 1.6\sigma^{**}$		
GA 44030	2300°C-4 hr.	19.9	13.1	15.9	1.1
GA 44031	2300°C-4 hr.	20.7	16.3	16.3	0.3
GA 44034	2300°C-4 hr.	20.8	17.2	17.3	0
UC 43003	As-received	20.3	12.3	17.1	0
UC 43004	As-received	22.2	5.3	18.9	0
UC 43004	2300°C-4 hr.	15.9	6.3	11.8	1.8
UC 43005	As-received	25.1	14.6	20.7	0
UC 43005	2300°C-4 hr.	20.1	8.9	14.4	4.1
UC 43005	2300°C-4 hr.	17.2	5.2	12.9	2.9
UC 43006	As-received	22.0	9.7	16.0	2.3
UC 43006	2300°C-4 hr.	15.8	4.4	11.0	3.4
UC 43006	2300°C-4 hr.	16.8	6.8	11.6	4.5
UC 43007	As-received	20.4	11.3	15.2	0.3
UC 43007	2300°C-4 hr.	14.1	5.3	9.4	2.0
UC 43008	2300°C-4 hr.	15.0	3.8	11.0	4.2
UC 43008	2300°C-4 hr.	11.8	2.2	9.2	4.7
UC 43009	2300°C-4 hr.	13.7	5.4	10.3	1.0
UC 43009	2300°C-4 hr.	13.0	6.7	10.0	0.6
UC 43010	2300°C-4 hr.	16.7	7.6	13.9	0
UC 43011	As-received	21.1	--	18.7	0.8
UC 43011	2300°C-4 hr.	18.5	8.6	14.4	0.3
UC 43011	2300°C-4 hr.	14.7	6.7	11.2	1.8
UC 43012	As-received	21.4	--	18.1	0.8
UC 43012	2300°C-4 hr.	16.4	7.8	12.6	0.9
UC 43012	2300°C-4 hr.	16.2	7.2	11.8	3.2
UC 43013	As-received	22.2	--	19.5	0.2
UC 43013	2300°C-4 hr.	17.8	8.4	15.8	1.5
UC 43013	2300°C-4 hr.	16.4	6.7	12.3	4.3
UC 43014	2300°C-4 hr.	17.9	10.3	14.5	5.5
UC 43014	2300°C-4 hr.	21.2	14.0	17.0	3.3
UC 43015	As-received	21.8	--	19.4	0.9
UC 43015	2300°C-4 hr.	19.4	10.3	15.9	1.8
UC 43015	2300°C-4 hr.	16.3	7.7	11.5	8.0
UC 43016	As-received	22.5	14.6	19.5	0
UC 43016	2300°C-4 hr.	16.6	7.0	12.3	9.8
UC 43016	2300°C-4 hr.	20.9	13.8	16.9	6.0
UC 43016	2300°C-4 hr.	15.8	6.2	12.6	13.0
UC 43017	As-received	24.1	14.4	20.1	0.6

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Table I Cont'd.

Sample	Test Condition	$\bar{X}$ = Avg. Coating Thickness		Min. Coating Thickness	% Particles Migrated
		$\bar{X}$	$\bar{X}-1.6\sigma^{**}$		
UC 43017	As-received	21.8	12.2	17.6	0
UC 43017	2300°C-4 hr.	17.8	8.5	14.1	3.5
UC 43017	2300°C-4 hr.	17.0	8.0	12.8	2.9
UC 43017	2300°C-4 hr.	18.8	9.1	13.5	2.9
UC 43018	2300°C-4 hr.	16.5	8.3	12.1	3.1
UC 43018	2300°C-4 hr.	21.1	12.5	16.9	2.8
UC 43019	As-received	21.8	13.9	19.3	1.2
UC 43019	2300°C-4 hr.	20.2	10.3	17.5	5.3
UC 43019	2300°C-4 hr.	19.8	12.0	15.7	4.3
UC 43019	2300°C-4 hr.	19.2	8.6	13.9	3.8
UC 43020	2300°C-4 hr.	20.6	11.3	16.1	3.6
UC 43021	2300°C-4 hr.	18.6	9.1	16.1	2.8
UC 43022	2300°C-4 hr.	19.0	10.6	14.9	2.4
UC 43023	2300°C-4 hr.	21.1	11.6	16.0	1.9
UC 43024	2300°C-4 hr.	21.6	14.9	17.7	1.0
UC 43025	2300°C-4 hr.	19.0	10.2	16.0	1.4
UC 43027	2300°C-4 hr.	18.9	10.5	14.8	2.9
UC 43028	2300°C-4 hr.	20.1	11.1	15.1	2.8
UC 43029	2300°C-4 hr.	19.5	12.6	16.2	1.7
UC 43030	2300°C-4 hr.	22.7	15.3	19.9	1.3
UC 43031	2300°C-4 hr.	19.2	11.2	15.3	3.2

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coating thickness and $\bar{X}-1.6\sigma$ performance of the Union Carbide material shows a wider spread than the GA lots. The $\bar{X}-1.6\sigma$ ranged from 22-15.3 μ and average coating thickness from 11.8-25.1 μ .

The data reported in Table I is cumulative only through February 15. Data on later lots, not available at this writing, show great improvement in Union Carbide particles and maintenance of excellent performance by General Atomic particles.

Work has continued on evaluation of production fuel materials under 2500°C-1/2 hr. thermal test conditions to determine capability of meeting future operational requirements necessitating higher fuel temperatures. The results of these tests are included in Table II. An erratic pattern of performance, as measured by total particles migrated, is evidenced by the data. Both General Atomic and Union Carbide materials show from 1% to essentially 100% total migration, depending on individual lots. Why some lots should behave in an excellent manner, and others completely fail, cannot be determined at the present time. The method of heat treatment and the measurement of temperature during heat treatment are rigidly controlled in the laboratory, and cannot be contributing to the wide variations exhibited by the samples. A few re-runs of several samples resulted in approximately the same values of total migration being observed as in the original cases. Attempts will be made to relate coating structure, core-coating interface, and coating thickness to migration behavior on lots showing widely divergent behavior.

Thermal cycling studies have also been continued, using the procedure

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TABLE II

Thermal Migration Tests at Temperature of 2500°C for 1/2 Hour

Sample	$\bar{X}$ = Avg. Coating Thickness	Min. Coating Thickness	% Particles Migrated
	(μ)	(μ)	
GA 44003	10.5	6.9	52.4
GA 44004	21.0	18.1	1.4
GA 44004	--	--	95.
GA 44005	19.4	16.1	7.0
GA 44006	20.2	17.0	8.4
GA 44007	24.2	20.3	6.7
GA 44008	--	--	88.3
GA 44009	--	--	83.6
GA 44010	26.1	21.5	9.9
GA 44011	--	--	50.8
GA 44012	--	--	90.
GA 44013	--	--	70.0
GA 44014	--	--	90.
GA 44015	--	--	90.
GA 44016	--	--	58.3
GA 44017	--	--	78.8
GA 44018	--	--	67.0
GA 44019	--	--	21.2
GA 44020	--	--	28.1
GA 44022	--	--	6.4
GA 44023	18.9	14.4	17.8
GA 44025	21.1	16.7	9.2
UC 43003	15.8	11.9	5.9
UC 43004	14.3	10.2	13.6
UC 43005	16.2	12.1	2.4
UC 43006	12.0	8.3	26.0
UC 43007	11.7	7.9	33.8
UC 43008	--	--	100.
UC 43009	--	--	100.
UC 43010	--	--	90.
UC 43011	--	--	38.2
UC 43012	--	--	100.
UC 43013	6.4	4.2	63.7
UC 43014	--	--	90.
UC 43015	--	--	46.8
UC 43016	--	--	52.2
UC 43018	--	--	37.6
UC 43019	20.5	14.8	14.7

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Table II Cont'd.

<u>Sample</u>	$\bar{X}$ = Avg. Coating Thickness	Min. Coating Thickness	<u>% Particles Migrated</u>
	<u>(μ)</u>	<u>(μ)</u>	
UC 43020	--	--	53.5
UC 43021	--	--	100.
UC 43022	20.3	16.5	1.4
UC 43023	21.7	17.5	2.0
UC 43024	16.8	9.9	21.3
UC 43025	20.2	15.2	3.7

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described in the previous meeting report. One of the aims of the cycling test is to determine if migration resistance can be improved in the coating by progressively altering structure through a series of thermal cycles. These cycles may produce beneficial effects on the coating structure due to uranium migration, when the cycles are conducted over many short time intervals. Results of these cycling tests on four development type samples during the past report period are listed in Table III. These results repeat the experience found with earlier samples, namely that no measurable particle deterioration occurs as a function of the thermal treatment. However, when the treated materials were exposed at 2500°C for 1/2 hour, the same inconsistent pattern of migration occurred. The Y-12 sample was 100% migrated. The 3M sample showed very low migration, despite a very thin coating. One of Union Carbide's samples showed excellent resistance to migration, while the other was 75% migrated.

MECHANICAL DAMAGE STUDIES (W. F. Brizes)

Previously reported data indicate that a maximum of 0.4 w/o uranium is leachable from the first stages of element fabrication, i.e., up to the final extrusion process. To determine if mechanical damage is occurring to fuel particles beneath the element surface during the 2nd stage of fuel element fabrication (cure, bake, graphitization, machining, and high temperature leach), samples were taken from each of the above steps and leached at 90°C in a 1N HNO₃ solution for 4 hours to remove any uranium from damaged particles

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TABLE III

Thermal Cycling Tests - Development Samples

Sample	Test Condition	$\bar{X}$ = Avg. Coating Thickness		Min. Coat Thickness	% Particles Migrated
		$\bar{X}$	$\bar{X}-1.6\sigma$		
Y-12 Li 111C ⁽¹⁾	2300°C	28.9	22.4	22.9	0
	7 cycles	29.3	22.9	23.6	0
	at 1/2 hour each	29.0	22.7	24.0	.6
	followed by	29.4	24.0	24.6	0
	↓	28.0	21.5	21.2	.5
		27.8	19.7	22.3	0
		28.5	21.2	21.9	.6
	2500°C-1/2 hr.	--	--	--	100
3M-LASL 588 ⁽²⁾	2300°C	13.6	9.2	12.3	0.7
	7 cycles	13.0	9.5	11.8	0.8
	at 1/2 hr. each	13.3	10.4	12.2	1.3
	followed by	13.6	8.7	12.4	1.0
	↓	14.0	11.0	11.8	2.1
		13.8	9.4	12.3	0.9
		13.9	10.7	11.7	0.7
	2500°C-1/2 hr.	12.9	9.3	10.7	3.4
UC-D49A ⁽³⁾	2300°C	20.8	16.2	17.9	0
	7 cycles	20.3	14.2	16.9	1.6
	at 1/2 hr. each	19.4	13.9	15.8	2.3
	followed by	17.8	12.0	13.4	0.4
	↓	18.3	11.7	14.3	2.6
		17.7	11.6	13.3	1.7
		17.0	10.5	12.0	1.1
	2500°C-1/2 hr.	--	--	--	75.6
UC-D54A	2300°C	18.7	13.6	15.8	1.4
	7 cycles	19.1	14.7	16.1	0
	at 1/2 hr. each	19.2	13.4	16.8	.6
	followed by	19.6	15.8	17.0	.6
	↓	20.2	14.7	17.6	0
		19.5	14.7	18.0	0
		20.9	16.3	17.3	0
	2500°C-1/2 hr.	19.3	16.2	17.7	1.7

- (1) Y-12 (Union Carbide-Oak Ridge)
(2) 3M material submitted to Los Alamos
(3) UC (Union Carbide - Lawrenceburg, Tenn.)

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on the surface. The sample was then anodically decomposed by placing it at the anode in a 1N HNO₃ solution (16 volts, 10 amps). The interior particles were then leached at 90°C in the same solution for 2 hours. The analysis of the leach solution indicated a maximum of 1% damage to fuel particles below the element surface during the machining operation. This is considered an acceptable loss. Only material from one vendor was used for mechanical damage studies during the second stage of fuel element fabrication but it can be considered representative of all vendors. The results of this treatment are shown in Table IV.

FUEL PARTICLE COATING DEVELOPMENT (A. L. Feild, Jr.)

Like other organizations engaged in the study and development of improved fuel particles, WANL has put forth a modest effort directed toward improving UC₂ particle coating technology. Although WANL's prime function has been the evaluation of development and production vendor fuels, employment of an unusual approach to producing improved high temperature coatings has resulted in preliminary batches of fuel particles showing better migration resistance at 2500°C and 2600°C than the best conventionally PyC coated commercial particles. This work to date is far from complete, but sufficient data have been generated to consider bringing the process to a state of commercial feasibility.

Our work during the past year with a small laboratory fluid bed furnace demonstrated the ability to produce duplex pyrocarbon coatings of controlled density, structure, and thickness which would meet the thermal migration

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TABLE IV

Uranium Leachable From an Anodically Dissolutioned Element

Element #89-21548

<u>Sample</u>	<u>% U Leachable by 1N HNO₃ at 90°C for 2 hours</u>
As-extruded	0.29
As-cured	0.08
As-baked	0.03
As-graphitized	0.40
As-machined	0.92
As-leached	0.53

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requirements of WANL-PDS-30050-B. However, none of these coatings or the coatings on production lots of particles exhibited reproducible satisfactory migration behavior at 2500°C in a 1/2 hour test. It seemed that a different approach was necessary to permit fuel operating temperatures above the melting point of UC₂ (2450°C) for extended time periods.

Two approaches have been tried experimentally. The first involves the addition of zirconium to the outer portion of the PyC coating, by means of controlled addition of ZrCl₄ vapor to the methane-helium stream in the fluid bed particle coater. The second consists of using aluminum for the additive, introducing it to the methane-helium stream in the form of AlCl₃ vapor. Considerably more work has been done on the former technique, although the latter appears to offer promise in restricting uranium migration by means of a different mechanism.

In the co-deposition of Zr, the inner laminar coating of pure PyC and up to 10 μ thick, is deposited at low temperature and is of moderate density. The coating temperature is then raised, and gas flows adjusted to produce a high density coating of granular structure, 10-15 μ thick containing a small Zr addition. A number of evaluation techniques have been used in an effort to determine the effects of Zr on the thermal migration behavior, and to study the mechanism by which the Zr-doped PyC coating enhances migration resistance. These analytical tools have included micro-radiography, metallography, chemical analysis, electron microprobe, x-ray diffraction, and electron microscopy.

For determination of migration resistance, and comparison with current

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vendor particles, Figures 1-7 show microradiographic results of GA, UC, and WANL particles under different thermal exposure conditions. All particles behave well under the 2300°C-4 hr. treatment (WANL-PDS-30050-B). At 2500°C for 1/2 hr. the GA and UC materials show high total migration, while the WANL Zr-doped particles (Lot 10A) exhibit no coating penetration. Even at 2600°C for 1/2 hr. a fair percentage of the WANL particle coatings are still resisting uranium penetration. More recently, a sample of Lot 10A material was exposed at 2500°C for 2 hours and showed no total migration through the coating. The radiographic interpretation of the Zr-doped coatings causes problems, because of the relatively high x-ray absorption coefficient of the Zr. Thus, it becomes difficult to determine the true uranium migration in PyC due to the absorption effects of the Zr present in the coating.

In efforts to minimize this problem, higher x-ray voltages are being used (up to 30kv) to delineate the core material, but residual PyC coating will then not show up on the radiographic plate. Another feature noticeable in these radiographs is the variation in thickness of the coatings on different size particles. This is primarily a function of fluid bed operation, which presents control problems when small charges (10g) are used. Larger charges are now being used in the hope that uniform particle fluidity in the bed can be achieved, thereby yielding particles with uniform coating thicknesses and similar structures. This problem is pointed out more clearly in the set of photomicrographs (Figure 8-10) which are 400X pictures of WANL migration resistant particles after 2500°C and 2600°C 1/2 hour treatments (Lot 10A). Two particles from the same coating batch (Figure 9-10) show different coating thicknesses

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and different coating structures, although both appear to be migration resistant.

Gravimetric analyses of each of the Zr-doped coating runs, using two types of particles, are reported in Table V. These runs were conducted at slowly increasing ZrCl_4 flow rates from run to run, which should be reflected in increasing zirconium content of the coating. Such a pattern generally exists, although the Zr analysis on Run 13A is inexplicably high and low Zr results on Runs 16A and 17A resulted from vaporizer channeling. Spectrophotometer analyses for Zr are now being conducted on these same samples to determine the accuracy of the gravimetric analyses.

Electron microprobe analyses on several as-coated particles from Runs 10A and 13A were made. Traces from the center of the core to the surface of the coating were obtained, providing quantitative analyses of uranium and zirconium as a function of radial distance from the center of the particle. On Run 10A, the Zr content in the coating averaged less than twice the background value (0.5%), and increased slightly from the core to the coating surface. This value approximates the 1% Zr found by chemical analysis, if it is assumed that all the Zr is located in the coating, a logical assumption since only background was present in the core. On Run 13A, the Zr content peaked up rapidly near the core-coating interface to approximately 50-60% Zr, and then gradually diminished in the direction of the coating surface to a value near 5%. Again, the agreement with a chemical analysis of 20% Zr in the particles is fair, if one assumes all the Zr in the coating, with an average saturation level midway between 5% and 50% across the coating thickness. Again only background

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TABLE V

Chemical Analyses on Zr-Doped Coatings*

<u>Sample No.</u>	<u>w/o U</u>	<u>w/o Zr</u>		<u>Coater Flow Conditions</u>
10A	67.61	0.99	Vendor A**	500cc/min thru $ZrCl_4$ vaporizer
11A	71.92	2.65		550cc/min thru $ZrCl_4$ vaporizer
12A	70.52	3.54		600cc/min thru $ZrCl_4$ vaporizer
13A	49.41	19.94		650cc/min thru $ZrCl_4$ vaporizer
14A	73.49	1.30	Vendor B***	500cc/min thru $ZrCl_4$ vaporizer
15A	76.19	3.57		550cc/min thru $ZrCl_4$ vaporizer
16A	73.34	2.37		600cc/min thru $ZrCl_4$ vaporizer
17A	79.97	1.82		650cc/min thru $ZrCl_4$ vaporizer

* Total Zr and U in coated particle sample

** Uncoated particles supplied by Vendor A

*** Uncoated particles supplied by Vendor B

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WANL-TME-1167

Zr was found in the core. It is difficult to interpret why the Zr concentration is heavier in the inner coating layers, except that some Zr migration could have occurred because of the thin inner coating (5-6 μ) of these particles. The uranium migration due to the high temperature outer coating step was negligible, as shown by minor penetration of uranium into the lower density, low temperature inner coating. It is planned to submit particles treated at 2500°C and 2600°C to the same type of analysis to determine the effects on zirconium and uranium behavior.

X-ray diffraction studies on samples from Runs 10A, 11A, 12A, and 13A were conducted, using both as-coated particles and particles heat treated at 2500°C for 1/2 hr. Attempts were made to determine the extent of solid-solution alloying of ZrC and UC in the coating and to ascertain effects of the Zr and U on graphitization of the PyC coating. The results are shown in Table VI. Indications are that the 2500°C-1/2 hr. heat treatment causes the PyC coating to undergo some graphitization, as evidenced by a decrease in the "C" parameter. Apparently the Zr and/or U act as catalysts to promote graphitization. Also, there is a solid solution existing between UC and ZrC in the heat treated particles, containing from 12-17 at/o UC. These two effects could be expected to provide increased migration resistance, based on prior WANL work with highly graphitic particle coatings and uncoated mixed carbide fuel materials.

Electron microscopy analysis was used in an effort to detect a second phase in the PyC coating of as-coated particles. Samples from Run 10A and Run 13A, representing wide variations in Zr content, were used. Even at 8000X (1/4 μ resolution), no definite precipitate could be identified, although

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TABLE VI

X-ray Diffraction on Zr-Doped PyC Coatings

Run	Phases	As-Coated		2500°C-1/2 hr.	
		Whole	Crushed	Whole	Crushed
10A	PyC ("C" Parameter) a/o UC in ZrC	3.43 Å -	3.43 Å -	3.38 Å* -	3.38 Å* -
11A	PyC ("C" Parameter) a/o UC in ZrC	3.42 Å 0	3.42 Å ~1-2	3.37 Å 15	3.37 Å 17
12A	PyC ("C" Parameter) a/o UC in ZrC	3.42 Å 0	3.42 Å ~1-2	3.37 Å 15	3.37 Å 17
13A	PyC ("C" Parameter) a/o UC in ZrC	3.43 Å 0	3.43 Å ~1	3.36 Å 12	3.36 Å 13

* Split peaks - difficult to resolve

- Not resolved

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there was more of some type of random coating defect structure visible in the sample containing the higher Zr content. No form of a dispersed single carbide could be found. This indicates that either the dispersion is finer than can be resolved at this magnification, the additive in the coating is dissolved in the PyC or is combined with UC as a solid solution carbide whose structure cannot be resolved. The last possibility seems remote for as-coated materials, based on the fragmentary x-ray data gathered thus far.

With regard to the addition of aluminum to the PyC coating, only one run has been made but others are planned. In this run, AlCl_3 was vaporized and fed into the CH_4 -He coating stream at a partial pressure around 5mm. A coating approximately 10μ thick (less than desired) was formed. X-ray diffraction analysis showed no residual Al or Al_4C_3 in the coating. However, the outer $1/3$ of the coating showed a decrease in "C" parameter from $3.41 \text{ \AA}$ to $3.36 \text{ \AA}$, theoretical for graphite. A sample of these particles was exposed at 2500°C for $1/2$ hour and the migration resistance was very good. At 2600°C for $1/2$ hour complete failure of coatings occurred, but this may be partly related to the thinness of the originally deposited coating. It appears that the catalytic effect of Al in graphitizing the PyC coating effectively increases the migration resistance, even though the Al is a fugitive additive.

FIGURE 1 CP 43005 2300°C - 4 HR. 7 KV X-RAY

FIGURE 2 GA 44009 2300°C - 4 HR. 7 KV X-RAY

FIGURE 3 WANL 2300°C - 4 HR. 15 KV X-RAY

FIGURE 4 CP 43013 2500°C - ½ HR. 7 KV X-RAY

FIGURE 5 GA 44008 2500°C - ½ HR. 7 KV X-RAY

FIGURE 6 WANL 2500°C - ½ HR. 15 KV X-RAY

FIGURE 7 WANL 2600°C - 1/2 HR. 15 KV X-RAY

FIGURE 8 WANL 2500°C - ½ HR.
MICRO (400X)

FIGURE 9 WANL 2600°C - ½ HR.
MICRO (400X)

FIGURE 10 WANL 2600°C - ½ HR.
MICRO (400X)

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84

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