UNC-5003

CARBIDE FUEL DEVELOPMENT

Progress Report

Period of September 15, 1961 to December 31, 1961

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February 9, 1962

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FOREWORD

The Carbide Fuel Development project is part of the AEC Fuel Cycle Development Program. The prime contractor is the United Nuclear Corporation, Development Division, formerly Nuclear Development Corporation of America (NDA), and the subcontractor is The Carborundum Company. The United Nuclear Corporation is performing the conceptual design, fuel evaluation, fuel irradiation, and irradiated fuel examination. The Carborundum Company is fabricating the fuel. Both companies are operating plutonium handling facilities.

The report covers progress from September 15, 1961 to December 31, 1961. Previous progress was reported in:

NDA 2140-2, Carbide Fuel Development — Phase I Report (Oct. 15, 1959)

NDA 2145-1, Carbide Fuel Development — Progress Report (Mar. 11, 1960)

NDA 2145-4, Carbide Fuel Development — Progress Report (June 13, 1960)

NDA 2145-5, Carbide Fuel Development — Progress Report (Aug. 30, 1960)

NDA 2145-6, Carbide Fuel Development — Phase II Report (Nov. 6, 1960)

NDA 2162-1, Carbide Fuel Development — Progress Report (Feb. 28, 1961)

NDA 2162-3, Carbide Fuel Development — Progress Report (June 1, 1961)

NDA 2162-5, Carbide Fuel Development — Phase III Report (Sept. 30, 1961).

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1. INTRODUCTION

Fuel made of a combination of UC and PuC has a potential of reducing the fuel cycle cost of existing fast breeder reactors. The fuel cycle cost reduction is anticipated because of increased burnup and increased power generation capability of UC-PuC, compared to presently available metallic fuels. The effect of high burnup and high power generation rate on the stability of UC-PuC is not known. However, UC irradiation tests show that carbide fuels are dimensionally more stable than metallic fuels. Because of the high melting point and good thermal conductivity of UC and the formation of solid solutions of UC-PuC with high melting points, there is further expectation that carbide fuels will be capable of high power generation rates.

The Carbide Fuel Development Program is concerned with the technology of the entire UC-PuC fuel cycle. The major goal of the program is to produce UC-PuC and to obtain data on its irradiation behavior for long burnups and at high power generation rates. In addition, other areas of the fuel cycle are being explored to discover potential problems. The program was initiated in May 1959 and as originally outlined covers a period of about four and one-half years. Program objectives are outlined below.

Conceptual Design

1. An analytical study of the effect of substitution of UC-PuC on heat transfer, physics, and cost of existing fast breeder reactors.

2. Conceptual design of rod-type, fuel element configurations which can be substituted directly in existing reactors.

The above was completed and was reported in NDA 2140-2.

Facility Design and Fabrication

1. Design and construction of a facility for carbide fabrication at The Carborundum Company.

2. Design and construction of a facility for carbide evaluation at United Nuclear.

The above was completed and reported in NDA 2145-6.

Fuel Fabrication and Evaluation

1. Explore various methods for preparation of fuel from powders and its fabrication into cylindrical pellets. High density (up to 13.1 g/cm^3) UC and UC-PuC pellets have been made.

2. Evaluate pellets by density measurement, chemical analysis, x-ray diffraction, hardness, metallography and fuel-cladding compatibility studies. This is complete for UC and initiated for UC-PuC. The UC-PuC studies will also include melting point, thermal stability, and coefficient of expansion measurements.

Fuel Irradiation

1. Irradiate clad fuel samples with burnup and maximum fuel temperature as the major variables. A minimum 2% burnup of all fuel atoms by fission and a minimum 650 °C (1200 °F) central fuel temperature were selected to establish the economic advantages of the fuel. This is complete for UC, and experiments for UC-PuC are under construction.

2. Make a post-irradiation examination. This is in progress for UC.

Full Scale Fuel Assembly

Design and construct a full scale fuel element assembly for irradiation in an existing fast breeder reactor.

2. SUMMARY

2.1 FUEL FABRICATION AND EVALUATION

Single phase, solid solution, UC-PuC powder was synthesized reproducibly from a mixture of the oxides and carbon. A simple method of monitoring the reaction was developed. UC-PuC-0.1 w/o Ni pellets of 93% theoretical density have been made reproducibly, with some samples as high as 95% of theoretical density. The pellets contain minor amounts of $(U,Pu)_2C_3$ most of the time. Efforts to make reproducible 95%, single-phase material are under way.

Microprobe analysis of UC-0.1 w/o Ni specimens was completed. A second phase apparently promoted by the nickel was shown to be probably U_2C_3. Essentially all the nickel was found in solution in the matrix UC.

2.2 IRRADIATION TESTS

The post-irradiation examination of the UC specimens completed to date showed that the UC pellets had the same appearance after irradiation as before irradiation. Their dimensional changes were very slight (1.4% volume increase). Fission gas release was low and within the sensitivity of the initial measurement (3.5% max.). The average specimen burnup was 18,500 MW-d/tonne at an average maximum fuel temperature of 760 ℃ (1400 °F).

2.3 PLUTONIUM FACILITIES

The plutonium facilities continued satisfactory operation at zero contamination level.

3. FUEL FABRICATION AND EVALUATION

3.1 INTRODUCTION

The goal of the fabrication studies is to produce high density solid solutions of PuC and UC by powder fabrication techniques. A high physical density (about 95% of theoretical) is desired to minimize fission gas release, give a high fuel density, and highest possible thermal conductivity.

The goal of the evaluation tests is to identify the material by density measurement, chemical analysis, x-ray diffraction, and metallography. Additional out-of-pile tests of fuel-cladding compatibility, thermal stability, melting point, and coefficient of expansion will survey properties of interest for in-pile tests.

3.2 CARBIDE POWDER PREPARATION

UC-PuC solid solution powders have been synthesized by two methods:

1. $4 UO_2 + PuO_2 + 15C \rightarrow 5(U_{0.8}Pu_{0.2})C + 10 CO$

2. $2 PuO_2 + 7C \rightarrow Pu_2C_3 + 4 CO$

   $Pu_2C_3 + U + 7UC \rightarrow 10(U_{0.8}Pu_{0.2})C$
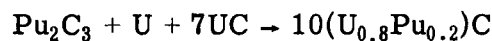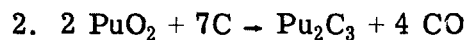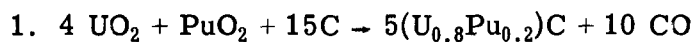
The powder produced by the two processes had essentially the same x-ray structure. The powder produced by the sesquicarbide route sintered to slightly lower densities than the powder produced from the mixed oxides. The sesquicarbide method has been abandoned since it does not offer any advantages, and requires two steps compared to the one step of the mixed oxide method. Work during the quarter concentrated on preparation of UC-PuC from the mixed oxides and the solid solution oxides.

The effect of the initial amount of carbon addition on the final structure of the powder was studied by synthesizing reaction mixes intended to form 100%, 95%, and 90% of the stoichiometric amount of carbon. The materials were synthesized from mixed oxides at 1500°C for 3 hr, and 1700°C for 1 hr. Results are shown in Table 1.

The starting material with 95% of stoichiometric carbon appears to be the most desirable since it eliminated the sesquicarbide. Lower carbon material may produce some undesirable zeta phase.

Pellets sintered from this powder showed a significant loss of plutonium (see Section 3.3).

The experiment using starting material with 95% of stoichiometric carbon was repeated with mixed oxides and performed with solid solution oxide powder. The solid solution powder was prepared by coprecipitation of peroxides and calcining, by Hanford Atomic Products Operations, and had the following analysis:

Pu/U_{nat} ratio	1/4	Pu^{241}	1.2%
Pu^{239}	90.7%	Pu^{242}	0.1%
Pu^{240}	7.9%		

The impurity content was a total of about 0.5%. The major impurities were:

Ca, Cr, Cu, Fe, in excess of 500 ppm (listed as 1000 ppm by HAPO)

	ppm		ppm
Na	500	Sn	160
Mg	385	Pb	50
Ni	275	Si	38
Mn	200	B	20

In comparison the mixed oxides had less than 300 ppm total impurities.

The results of the syntheses are shown in Table 2. Comparison of Experiment 1, Table 2 with Experiment 2, Table 1, indicates poor reproducibility of the final product. The high carbon content (theoretical 4.55% for 95% stoichiometric

Table 1 — The Effect of Carbon Content on the Syntheses of UC-PuC Powders
(Synthesized 1500 °C-3 hr; 1700 °C-1 hr)

Experiment No.	Intended Composition	Total Measured Carbon,%	X-Ray Analysis
1	$(U_{0.8}Pu_{0.2})C_{1.0}$	5.05	Major $(U,Pu)C$ Weak $(U,Pu)_2C_3$ (There appears to be a double UC-type phase)
2	$(U_{0.8}Pu_{0.2})C_{0.95}$	4.63	Single phase — $(U,Pu)C$ $a_0 = 4.964 \pm 0.001$ Å
3	$(U_{0.8}Pu_{0.2})C_{0.90}$	4.75	Single phase — $(U,Pu)C$ $a_0 = 4.964 \pm 0.001$ Å

Table 2 — Syntheses of UC-PuC Powders from Mixed Oxides and Solid Solution Oxides
(Synthesized 1500 °C-3 hr; 1700 °C-1 hr)

Experiment No.	Starting Material	Total Carbon in Product, %	X-Ray Analysis
1	UO_2, PuO_2, C	5.21	Major $(Pu,U)C$ Moderate $(Pu,U)_2C_3$ Weak $(Pu,U)O_2$
2	$(U,Pu)O_2, C$	4.75	Major $(Pu,U)C$ Weak/faint $(Pu,U)O_2$

mixture) of the powder from mixed oxides indicates an incomplete reaction. It could be explained on the basis that the PuO_2 used for experiments in Table 2 came from a different container than for those in Table 1. Although all of the PuO_2 powder used was made by the same source, same process, and at the same time, the PuO_2 used in experiments in Table 2 appeared coarser than the material from the previous container. The rate of reaction of the coarser material is likely to be slower.

Because the previously determined synthesis cycle did not appear to give a complete reaction with the second container of coarser PuO_2, a second experiment was initiated to determine the optimum reaction temperature to produce the composition $(U_{0.8}Pu_{0.2})C_{0.95}$ from the carbon reduction of the mixed oxides. Solid solutions were included for comparison. For this study, reaction mixes were heated to 1550 °C with hold times of from 5 to 8 hr followed by heating at 1625 °C and 1700 °C with hold times of 1 to 2 hr. Reacted pellets were crushed and repelletized between each reheat. The results of these experiments are summarized in Table 3. Carbon contents are shown following the treatment at each of the three temperatures used.

The results showed that a synthesis cycle with a maximum temperature of 1625 °C could give material which was completely reacted. This lower maximum temperature is desired to reduce plutonium losses as discussed in Section 3.3.

A series of experiments was run to condense the multi-step cycle into one treatment. For this series, 16-gram reaction batches were heated to 1625 °C and held at temperature for periods of 1/2, 1, and 2 hr. The reaction products were crushed and analyzed. The residual powders were then compacted without binder, and reheated to 1625 °C with additional hold times of 1/2, 1, and 1/2 hr, respectively. Results appear in Table 4.

Some inconsistencies in the relationship of carbon content and x-ray pattern with synthesis time could not be explained.

Table 3 — Results of Additional Experiments to Produce $(U_{0.8}Pu_{0.2})C_{0.95}$ by Carbon Reduction of the Oxides

Experiment No.	Starting Material	Reaction Temperature, Time, and Total Carbon				
		1550 °C 5 hr Hold	1550 °C 8 hr Hold	1625 °C +1 hr Hold	1625 °C +1 hr Hold	1700 °C +1 hr Hold
1	UO_2, PuO_2, C	6.94	--	5.00	4.53*	--
2	$(U, Pu)O_2, C$	--	4.75†	4.75‡	--	4.44§

Results of X-Ray Analysis

*Major $(Pu, U)C$; faint $(Pu, U)O_2$ and $(Pu, U)_2C_3$ $a = 4.968 \pm 0.001$ Å
† Major $(Pu, U)C$; faint $(Pu, U)_2C_3$; weak $(Pu, U)O_2$
‡ Major $(Pu, U)C$; faint $(Pu, U)O_2$
§ Major $(Pu, U)C$; very faint $(Pu, U)O_2$

Table 4 — Results of Multistep Synthesis Experiments at 1625 °C to Produce $(U_{0.8}Pu_{0.2})C_{0.95}$ Monitored by Carbon Analysis

Experiment No.	Hold Time at 1625 °C	Total Carbon, %	X-Ray Analysis
1	1/2 hr	7.32	Major $(Pu, U)O_2$ Moderate $(Pu, U)C$ and $(Pu, U)_2C_3$ Indication of $(Pu, U)C_2$
2	1/2 hr + an additional 1/2 hr	4.91	--
3	1 hr	6.12	Major $(Pu, U)O_2$ Moderate $(Pu, U)_2C_3$ Very faint $(Pu, U)C_2$ Trace $(Pu, U)C$
4	1 hr + an additional 1 hr	5.12	--
5	2 hr	4.77	Major $(Pu, U)C$ Faint $(Pu, U)_2C_3$ $a_0 = 4.967 \pm 0.001$ Å
6	2 hr + an additional 1/2 hr	4.62	Major $(Pu, U)C$ Weak $(Pu, U)O_2$ and $(Pu, U)_2C_3$ $a_0 = 4.969 \pm 0.001$ Å

The results indicated that a holding time slightly in excess of $2\frac{1}{2}$ hr should give the desired 4.55 w/o C. This was confirmed by a single step treatment for $2\frac{1}{2}$ hr, which is shown in Table 5.

In order to have a more rapid and economical indication of the completion of the reaction than carbon analysis, the carbon monoxide was monitored during the reaction. A Mine Safety Appliance type carbon monoxide tester was connected to the exhaust line from the furnace, and the gas was sampled periodically. Blanks of the system gas and of the gas drawn from the furnace while held at 1625°C indicated 0.000% and 0.002% CO, respectively. The results of synthesis experiments monitored with the CO indicator are given in Table 5. Both batches produced the desired single phase, solid solution powder.

3.3 CARBIDE PELLET FABRICATION

Past work has shown that 0.1 to 0.2 w/o nickel is an effective sintering aid for UC-PuC powder. Work continued in attempting to define the fabrication conditions which would give maximum density and single-phase structure.

Additional data were obtained on pellets described in Table 3.8 of NDA 2162-5. The data are summarized in Table 6.

Sintering experiments were conducted with the 4 UC-1 PuC solid solutions produced from mixed oxides, having the intended compositions $(U_{0.8}Pu_{0.2})C_{1.0}$ and $(U_{0.8}Pu_{0.2})C_{0.95}$ (Experiments 1 and 2 respectively, Table No. 1). The addition of 0.1% nickel was made to the batch powders to aid in the densification process.

The size of the pellets was 0.224 in. in diameter by about 0.2 in. long. The temporary binder was 1/4 w/o Carbowax 6000 and the cold forming pressure was 30,000 lb/in² Pellets were sintered on a tantalum-lined graphite crucible in the graphite resistance furnace at 1550°C with a hold time of 1 hr. The atmosphere, as in all experiments, was helium. Results are shown in Table 7.

In this and some of the other experiments an apparent increase in total carbon content was noted during sintering. Very recently this has been traced to carbon pickup from graphite furnace components. A change to noncarbonaceous

Table 5 — Results of One-Step Synthesis Experiments at 1625°C to Produce $(U_{0.8}Pu_{0.2})C_{0.95}$
Monitored by CO Meter

Experiment No.	Batch Size, g	CO at End of Run, %	Time to Reach Respective % CO, hr	Total Carbon, %	X-Ray Analysis
1	50	0.005	$6\frac{1}{2}$	4.53	Single phase (U,Pu)C $a_0 = 4.965 \pm 0.001$ Å
2	15	0.007	$2\frac{1}{2}$	4.58	Single phase (U,Pu)C $a_0 = 4.965 \pm 0.001$ Å

Table 6 — Effect of 0.1% Nickel Additions on the Sintering of UC-PuC
(Time at Maximum Temperature, 1 hr)

Material Density and Chemical Analysis

Experiment No.	Sintering Temp, °C	4UC-1PuC			4UC-1PuC + 0.1% Ni		
		Density, g/cm³	X-Ray Analysis	Total Carbon,%	Density, g/cm³	X-Ray Analysis	Total Carbon,%
1*	1350	10.07			12.26		4.75
1a†	1350	9.56		4.72	12.24		4.71
2*	1450	10.61		4.74	12.75		4.77
2a†	1450	9.89		4.74	12.59		4.82
3*	1550	11.77	Major MC Weak M_2C_3 4.964 Å	4.59	12.97	Major MC Weak M_2C_3 4.964 Å	4.79
3†	1550	11.77	Major MC Weak M_2C_3 4.961 Å	4.73		Major MC Weak M_2C_3 Faint MO_2 4.965 Å	4.77
4*	1650	12.06		4.64	12.75		4.79
4a†	1650	12.10		4.71	12.72		4.77
5*	1750	-		-	12.81		4.73
5a†	1750	12.20		4.66	12.75		4.81
6*	1350- 1 hr plus	12.11		4.65	-		-
6a†	1750- 1 hr	12.23		-	-		-

*4UC-1PuC solid solution from carbon reduction of the oxides to form $(U_{0.8}Pu_{0.2})C_{0.95}$ (theoretical 4.55 w/o C).

†4UC-1PuC solid solution synthesized from the reaction 7UC + U + Pu_2C_3 to form a stoichiometric composition (theoretical 4.80 w/o C).

Table 7 — Results of Sintering 4 UC-1 PuC-0.1 Ni Compositions
of Varying Carbon Content

Experiment No.	Sintering Temp and Hold Time	Density Range, g/cm³ (10 pellets)	Avg Density, g/cm³	Total Carbon,%
1*	1550 ℃ – 1 hr	12.38-12.50	12.43	5.25
2†	1550 ℃ – 1 hr	12.26-12.41	12.35	4.80

*Powder from Experiment 1, Table No. 1.
†Powder from Experiment 2, Table No. 1.

crucibles is being made; however, all results reported in this quarterly are based on sintering in tantalum-lined graphite crucibles.

An attempt is being made to identify and/or eliminate the light etching phase present in UC and UC-PuC compacts containing nickel. Annealing UC at 1850 ℃ in vacuum did eliminate the light phase, as shown in Figs. 1 and 2. A similar treatment was given to UC-PuC pellets to study the effect on microstructure, as well as on dimensions and weight. The results are shown in Table 8.

The results of metallographic examination of pellets from Experiment 1, Table 8, are shown in Figs. 3 and 4. The annealing treatment produced grain growth and more equiaxed grains; however, the light phase was still present in about the same quantity as before annealing. The annealing was done in a helium atmosphere (compared to vacuum for UC) and this is probably one reason for the difference in results between UC and UC-PuC. Metallographic examination did not show any difference between pellets made from powder prepared from mixed oxides and those made from powder prepared from sesquicarbide. The specimens in Figs. 3 and 4 were prepared for microprobe analysis and are currently being examined by Monsanto Chemical Company's Mound Laboratories.

The weight and dimensional changes are small, but consistent. The material being lost has not been identified; however, chemical analyses show that it is probably plutonium.

Table 8 — Effect of High Temperature Anneal on UC-PuC-0.1 Ni Pellets
(Pellets used are described in Tables 6 and 7)

| Experiment No. | Intended Composition | Before Anneal | | Expansion, % | | After 3 hr at 1750°C | |
		Sintering Temp, °C	Density, g/cm³	Diam	Height	Density, g/cm³	Weight Loss, %
1*	$(U_{0.8}Pu_{0.2})C_{0.95}$ +0.1% Ni	1550	12.41	0.16	0.06	12.34	0.252
2†	$(U_{0.8}Pu_{0.2})C_{1.0}$ +0.2% Ni	1550	12.86	0.21	0.92	12.70	0.304
3†	$(U_{0.8}Pu_{0.2})C_{1.0}$ +0.2% Ni	1450	12.79	0.36	0.61	12.48	1.15

*Powder made from mixed oxides.
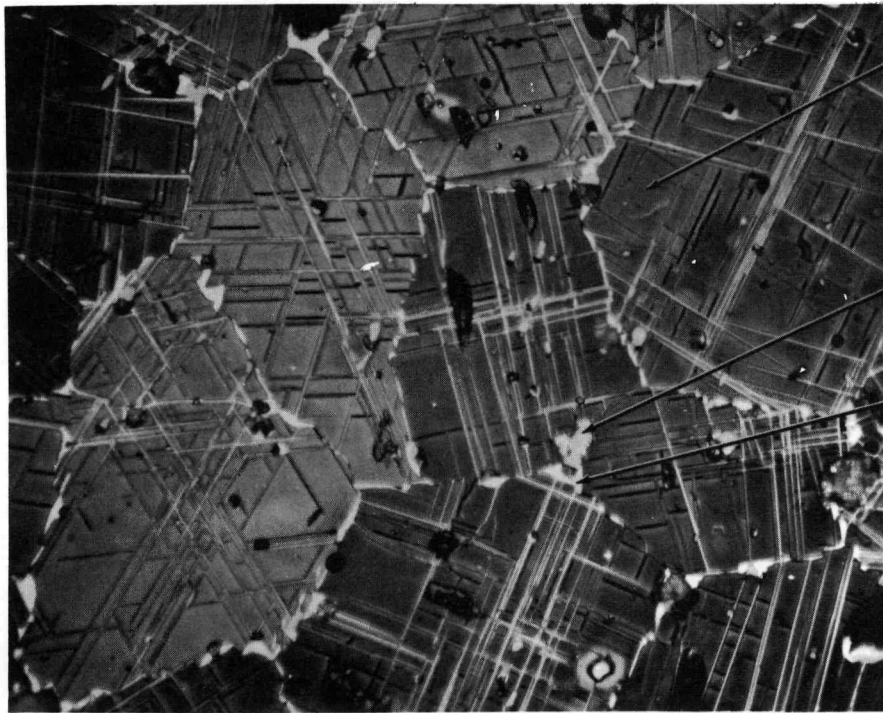† Powder made from sesquicarbide.
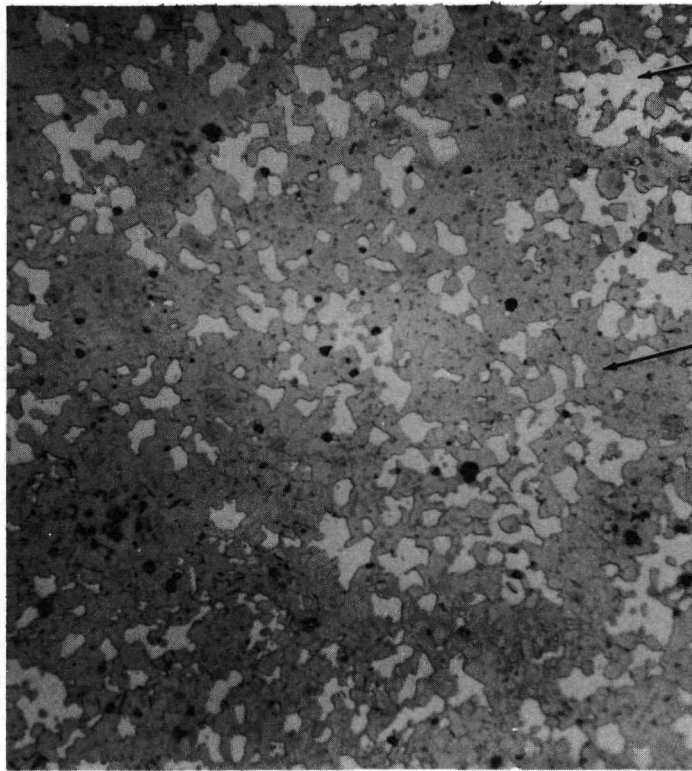
94.0±0.7% U
0.01 % Ni

95.0±0.7% U
0.19±0.01% Ni

Theoretical % U in:

UC	95.2
U₂C₃	93.0

Neg. No. 1299 D

Fig. 1 — UC-0.1% Ni sintered at 1525 °C, 4 hr —
500× — nitric acid–acetic acid–water etch

96.1±0.7% U
0.07±0.01% Ni

84.5±0.6% U
0.02±0.01% Ni

89.3±0.6% U
0.02±0.01% Ni

Theoretical % U in:

UC	95.2
U_2C_3	93.0
UC_2	90.8
UO_2	88.1
U_3O_8	84.8

Neg. No. 1297

Fig. 2 — UC-0.1% Ni sintered at 1525 °C, 4 hr, reheated at 1850 °C, 1 hr in vacuum — 500× – nitric acid–acetic acid–water etch
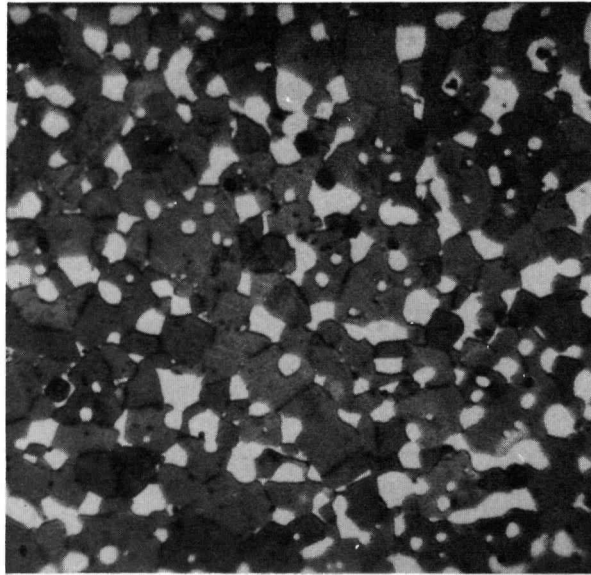
Neg. No. P12

Fig. 3 — Nominal 80% UC-20% PuC-0.1% Ni sintered at 1550 ℃, 1 hr (Exp. 1, Table 8) — 600× — nitric acid-acetic acid-water etch
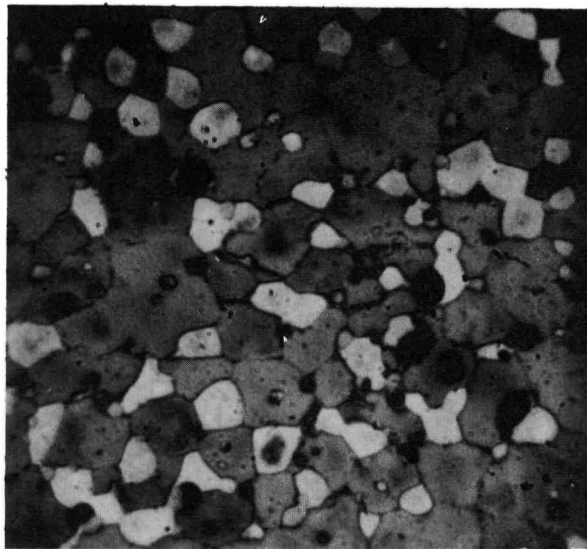
Neg. No. P10

Fig. 4 — Nominal 80% UC-20% PuC-0.1% Ni sintered at 1550 ℃, 1 hr; reheated at 1750 ℃, 3 hr in helium (Exp. 1, Table 8) — 600× — nitric acid-acetic acid-water etch

Chemical analysis of pellets from Experiment 1, Table 8, gave the following results:

	w/o U	w/o Pu
Sintered 1550°C, 1 hr	80.4	16.3
Sintered 1550°C, 1 hr; annealed 1750°C, 3 hr	81.8	16.1

Chemical analysis of the first, as sintered (1525°C, 4 hr) 4 UC-1 PuC-0.1 Ni pellet (Experiment 2, Table 3.7, NDA 2162-5) gave the following results:

Uranium	82.7 w/o (avg. of 3 analyses)
Plutonium	15.0 w/o (avg. of 5 analyses)
Carbon	4.4 w/o (avg. of 3 analyses)
Iron	0.08 w/o (avg. of 5 analyses)

The totals of the analyses add up to over 100%, indicating some inaccuracies in the analyses. The plutonium content, however, is significantly lower and the uranium content significantly higher than the original intended composition. The theoretical amounts of plutonium and uranium are 19% and 76%, respectively. This indicates that plutonium is lost during synthesis or sintering. A small amou of plutonium is being lost during annealing. The uranium analyses are being checked with new standards. * The plutonium analyses are being checked by the AEC's New Brunswick Analytical Laboratory. Samples from various stages of th synthesis cycle are being analyzed for plutonium to determine when the plutonium is being lost. The microprobe analyses will also given an indication of uranium and plutonium contents.

The pellets which show Pu loss were made from powder synthesized at a maximum temperature of 1700°C. A powder synthesis cycle with a peak temperature of 1625°C was developed. Chemical analyses of samples from this synthesis cycle are in progress. Difficulties are being encountered in the dissolution of PuO_2 and mixed carbides containing oxygen. A method of HF dissolution is being developed at United Nuclear and the New Brunswick laboratories.

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*The recently completed checks show the reported uranium analyses are 0.5% high.

Sintering experiments were made on the powder described in Table 2. Pressing and sintering procedures were the same as for the previous batch. The results are shown in Table 9.

Representative pellets from the 1550°C sintering experiment (Table 9) were weighed, measured and then heated to 1750°C for an additional hour to study the effects of high temperature on density, weight and dimensional changes. Results appear in Table 10. Metallographic examination of the pellets described in Table 10 will be made.

Sintering experiments were made on the single-phase powder described in Experiment 1, Table 5. Pressing and sintering procedures were the same as for previous batches. The results are shown in Table 11.

An investigation was made to determine the reason for the increase in total carbon. The cause was attributed to contamination of the milled powder by the bristles from the brush used to clean the ball mill and stainless steel balls. The brush bristles had become embrittled due to prolonged exposure to the dry helium atmosphere. Chemical analysis of the as-milled powder gave total carbon at 5.22%. This was the first instance where a brush was used to clean the ball mill. Future work will be done with a steel brush.

Subsequent sintering experiments will be made on material from Experiment 2, Table 5, which was not contaminated. If successful, another larger batch of powder will be synthesized.

3.4 MICROPROBE ANALYSIS

Microprobe analyses of "as-sintered" and sintered and annealed samples of UC-0.1% Ni were completed. The data are summarized in Figs. 1 and 2.

The best current estimate is that the light phase in the as-sintered specimen (Fig. 1) is U_2C_3 (or UC) with virtually no nickel in solution. The dark phase is conclusively UC with all of the nickel in solution. Nickel was not found as a metal or intermetallic compound.

Table 9 — Results of Sintering UC-PuC Made from Mixed and Solid Solution Oxides
(Powder from Table 2 sintered 1 hr at 1550 °C)

Material	Nickel Additive,%	Density Range, g/cm³	Average Density, g/cm³	Total Carbon,%
From Experiment No. 1, Table 2	None	11.70-11.94	11.77	5.02
(from mixed oxides)	0.1	12.11-12.26	12.19	--
From Experiment No. 2, Table 2	None	11.90-11.94	11.92	4.78
(from solid solution oxides)	0.1	11.90-12.06	11.96	--

Table 10 — Effects of High Temperature Anneal on Sintered UC-PuC Pellets

Experiment No.	Sintered 1 hr 1550°C		Annealed 1 hr 1750°C			
	Material 4UC-1PuC	Average Density, g/cm^3	Average Density, g/cm^3	Average Weight Loss, %	Total Carbon, %	X-Ray
1	From mixed oxides No Ni	11.8	12.3*	0.5	4.84	Major (U,Pu)C Moderate (U,Pu)$_2$C$_3$ Faint (U,Pu)O$_2$ $a_0 = 4.969 \pm 0.001$ Å
2	From mixed oxides 0.1% Ni	12.2	12.2†	0.2	5.15	
3	From solution oxides No Ni	11.9	Stuck to Ta liner‡		4.52	Major (U,Pu)C Weak (U,Pu)O$_2$ $a_0 = 4.984 \pm 0.001$ Å
4	From solution oxides 0.1% Ni	12.0			4.58	

*Average diameter and height shrinkage 1.7%.

†Average shrinkage negligible.

‡The analysis of the solid solution oxides showed a total impurity content of about 0.5 w/o. The high temperature reaction of these impurities with Ta may have caused sticking of the pellets.

Table 11 — Results of Sintering Experiments on Single-Phase UC-PuC Powder
(Powder from Experiment 1, Table 5)

Experiment No.	Intended Composition	Sintering Temp and Hold Time	Density Range, g/cm^3 (5 pellets)	Average Density, g/cm^3	Total Carbon,%
1	$(U_{0.80}Pu_{0.20})C_{0.95}$ +0.12 Ni	1550°C - 1 hr	(12.63-12.74)	12.68	4.99
2	$(U_{0.80}Pu_{0.20})C_{0.95}$	1750°C - 1 hr	(12.13-12.37)	12.29	5.04

The light phase in the sintered and annealed specimen (Fig. 2) has a different composition than the light phase in the as-sintered specimen. The best current estimate is that it is UO_2 (or UC_2). The grey phase is estimated to be U_3O_8. Virtually no nickel is in solution in either phase. Although spectral records were obtained on the white and grey phases, no additional detectable elements were noted. The dark phase is conclusively UC with about half the nickel still in solution. The remainder of the nickel has migrated to the grain boundaries, and some probably evaporated. Concentrations in excess of 40 to 50 w/o Ni were detected at the mutual interfaces of the white, grey, and matrix phases. The nickel enriched regions were much smaller than the electron beam size employed (the beam was 1 to 2μ) implying even greater concentrations of nickel than noted.

The nickel homogeneity in the dark areas was determined in an indirect way by measuring representative areas during the matrix analysis from one edge of the specimen to the other. All values were found to be within the expected statistical error of the single values noted.

The analyses were made by Advanced Metals Research Corp., on one of their own instruments. Composition determinations were made by the following procedure. The goniometer was aligned to record the characteristic line of a particular element such as NiKα. The electron beam was then positioned on an area of interest and the available x-ray intensity point counted. The intensity available from a pure element standard and the background intensity was also

carefully determined. At least ten different representative areas of each phase were studied and the intensity values averaged. In the case of $UL\alpha$, both a pure U standard and a pure UC were employed. The intensity ratio determined by comparing the intensity available from an area of interest to that from a pure element standard is a first order approximation to concentration in weight percent. This value was corrected for matrix absorption and fluorescence effects and the element concentration determined.

The following conclusions can be drawn from the analyses:

1. The nickel sintering aid is in solid solution in the as-sintered carbides. No low melting nickel alloys or compounds are formed which would be detrimental to the performance of the material as a high temperature fuel.

2. The nickel promotes the formation of a second phase, probably U_2C_3.

3. Annealing in vacuum at 1850 °C promotes diffusion of the nickel to grain boundaries, and probably subsequent evaporation.

4. The same annealing treatment also removes the second phase.

4. IRRADIATION TESTS

4.1 INTRODUCTION

In order for UC-PuC fuel to reduce fuel cycle cost, several conditions must be met. The fuel has to be able to achieve high burnup, high operating temperatures, and high power. At least 2 a/o burnup of all fuel atoms by fission is desirable at central fuel temperatures above 1200 °F (650 °C) with maximum dimensional stability of the fuel and minimum release of fission products. Power generation rate should be at least equivalent to that of presently planned fuels. The objective of the irradiation program is to determine whether the high burnup, temperature, and power density required can be achieved.

The irradiation tests measure temperatures, burnup, power generation rate, dimensional stability of the fuel, and fission gas release.

4.2 POST-IRRADIATION EXAMINATION OF UC SPECIMENS

The UC irradiation test, capsule W1-1, is currently being examined at the United Nuclear Hot Laboratory. A detailed description of the experiment and irradiation conditions were given in NDA 2162-5, pp. 29-41.

In summary, stainless steel and niobium-clad 24% enriched UC specimens were irradiated. Each specimen contained sixteen 0.191-in. diameter fuel pellets for an approximate 3-in. fueled length. The void space was filled with helium. The UC pellets were made by cold pressing and sintering UC powder, which in turn was made by reacting UO_2 with carbon. The average density of the pellets was

94% of theoretical. Irradiation conditions were 18,500 MW-d/tonne average burnup, 760°C (1400°F) average central fuel temperature, 315 w/cm (9.6 kw/ft) average heat generation rate, and 1.7 kw/cm^3 average power density.

During capsule disassembly the capsule inner shell was punctured and a gas sample taken to determine whether any fission gases had escaped the clad specimen. No activity could be detected in the gas sample bulb prior to sending it to Oak Ridge for mass spectrometer analysis for possible fission gases. Subsequent sectioning of the specimens did not reveal any sodium inside the cladding. The cladding and welds, therefore, remained leaktight throughout the experiment.

The diameter of both specimens was checked in numerous places and found to be identical to the dimensions prior to irradiation. The niobium-clad specimen had a slight bow (~1/64 in.); the stainless steel specimen was straight. The surface appearance of both specimens was the same as prior to irradiation. Fig. 5 shows a photograph of the clad specimens.

The cladding of both specimens was punctured to measure fission gas release. The internal gas volume was measured by a differential pressure gage, and gas samples were taken for mass spectrometer analysis. Fission gas release in the stainless steel-clad specimen was less than 3.5% (maximum sensitivity of experiment) based on pressure measurement. The pressure gage failed to function when the niobium-clad specimen was punctured. Gas samples were obtained from both specimens and sent to Oak Ridge for mass spectrometer analysis.

The cladding of both specimens was slit longitudinally. Fig. 6 shows the opened stainless steel cladding. The UC pellets were removed, examined visually, and measured.

The general appearance of the UC pellets after irradiation was the same as prior to irradiation, except that a third of the pellets were cracked into two or more pieces. The pellets were most probably cracked during handling in the hot lab.
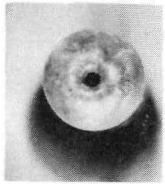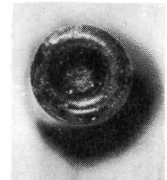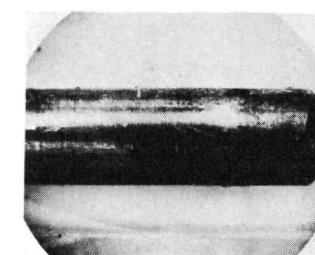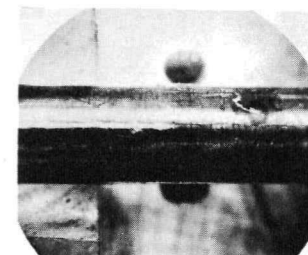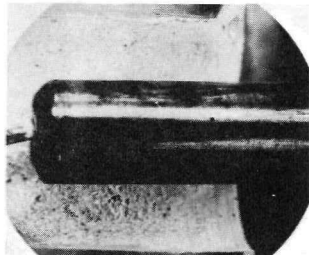
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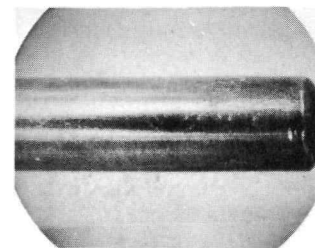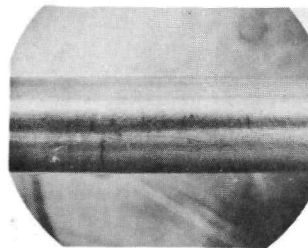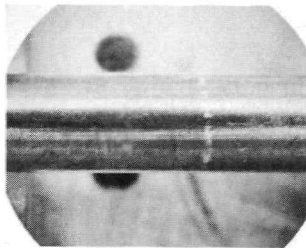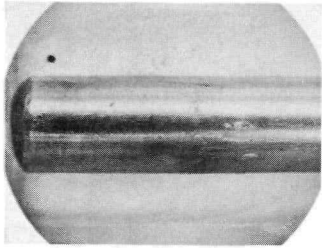
Capsule W1-1
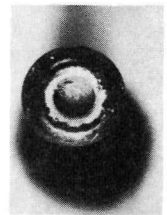Stainless steel clad specimen
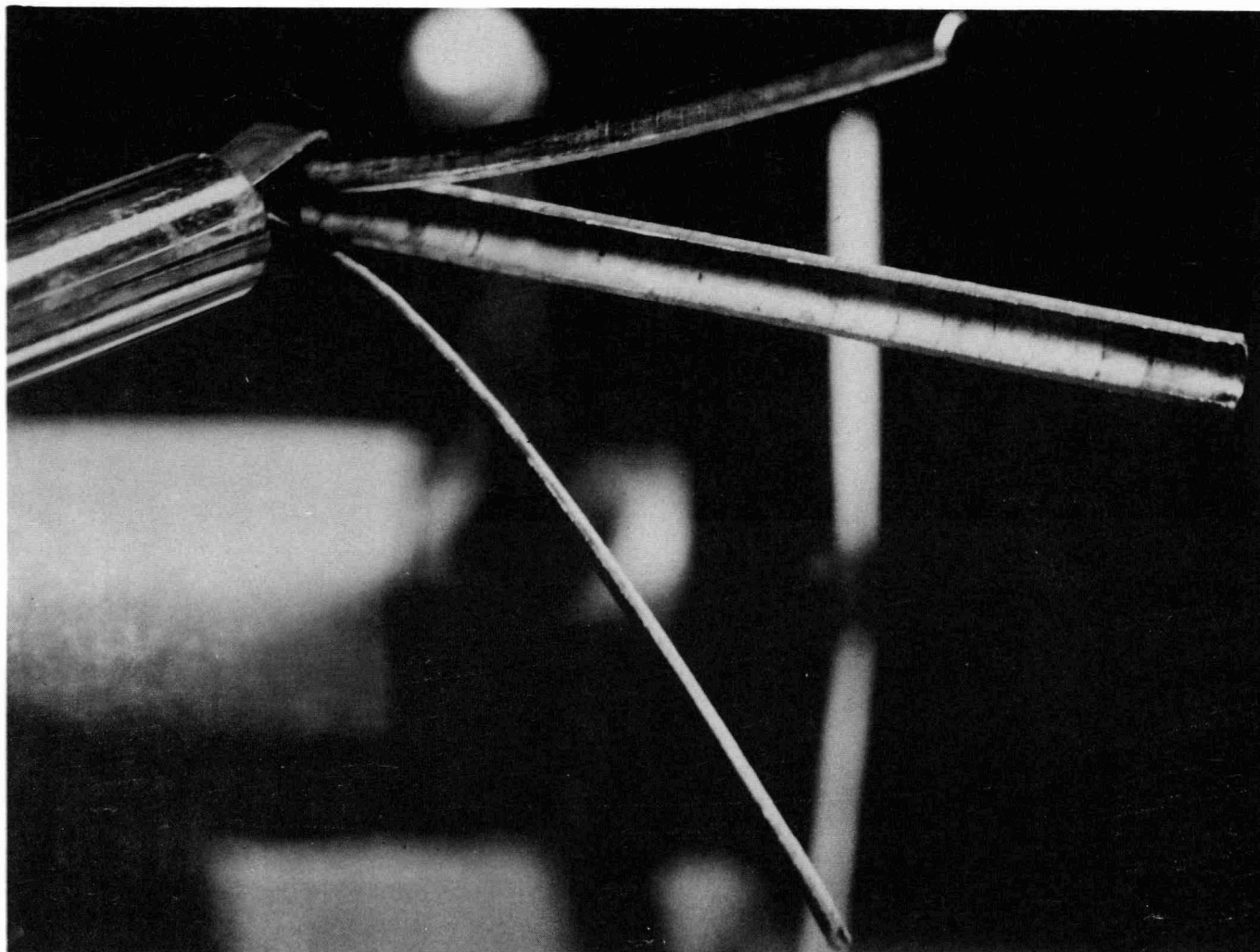
Plug
end

Thermo-
couple end

Capsule W1-1
Niobium clad specimen

Plug
end

Fig. 5 — Niobium and type 316 clad UC specimens
after irradiation

Neg. No. 3705

Fig. 6 — Type 316 cladding slit open for pellet
removal

A summary of the condition of the pellets after irradiation is:

Stainless Steel-Clad Specimen

15 pellets	One piece (Seven of the 15 pellets had a small incipient crack along a major diameter)
1 pellet	Cracked in two pieces

Niobium-Clad Specimen

|	
6 pellets	In one piece
2 pellets	Cracked in two pieces
1 pellet	Cracked in four pieces
7 pellets	Cracked in more than four pieces

The niobium-clad specimen was more difficult to disassemble and required more severe handling. This is probably the reason for the greater number of cracked pellets.

The fuel was considerably more brittle after irradiation. Fig. 7 shows a group of typical, uncracked pellets. The breaking of the edge around the central hole was probably caused by incipient cracks introduced during the pre-irradiation drilling operation. Fig. 8 shows pieces of a typical cracked pellet. Macro examination of the cross section and fractured pellet surfaces did not show any gross grain growth.

Measurement of the length and diameter of 14 whole pellets from the stainless steel clad specimen was completed (one pellet cracked during handling):

	Prior to Irradiation	After Irradiation
Avg. Diameter, in.	0.1910	0.1923
Avg. Length, in.	0.1833	0.1834

The 1-mil increase in diameter corresponds to a volume increase of 1.4%. The slightly increased diameter of the pellets corresponds to the ID of the clad-
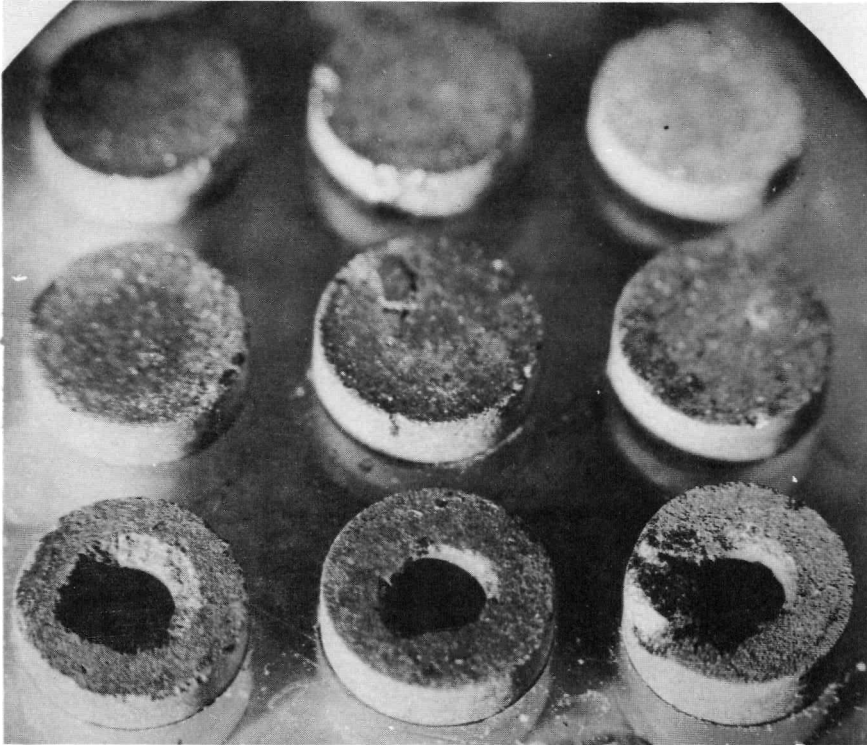
Neg. No. 3713

Fig. 7 — A group of whole irradiated UC pellets from the type 316 clad specimen. (Central hole was drilled prior to irradiation for thermocouple well.)
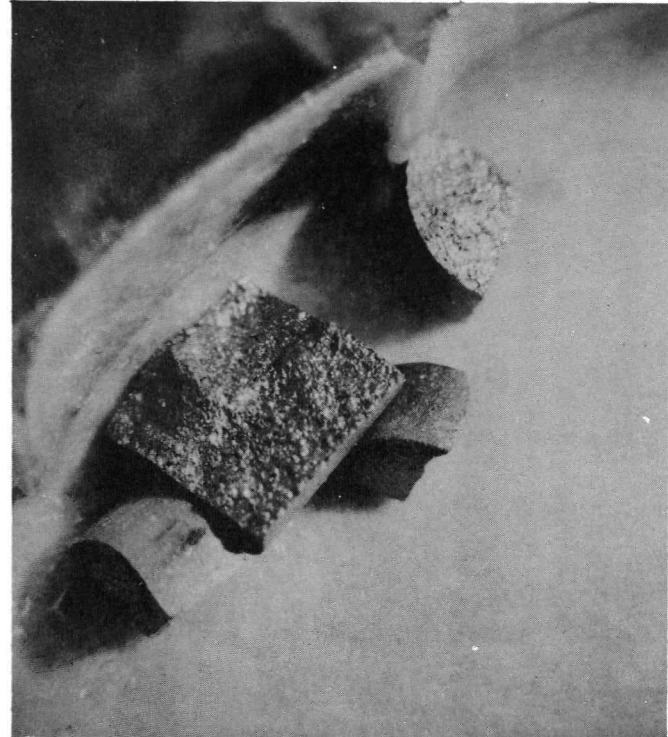
Neg. No. 3716

Fig. 8 — Typical cracked pellet from the niobium clad specimen

ding: 0.192 in. + 0.001 - 0.000. The examination is continuing and will be completed in the next quarter.

4.3 DESIGN FOR UC-PuC IRRADIATION TESTS

The basic design conditions for the UC-PuC irradiation tests were given on pp. 32-33, NDA 2162-5. Some modifications were made during the quarter.

The irradiation time of the 68,000 MW-d/tonne experiments was reduced from 21 months to 12 months by the substitution of 24% enriched uranium for natural uranium. Machine calculations of radial burnup and temperature distribution as a function of irradiation time were made. The calculations were based on non-uniform heat generation. Flux depression for highly enriched specimens in a thermal flux is considerable. For instance, for the 68,000 MW-d/tonne average specimens, the burnup will be distributed as follows:

	MW-d/tonne
Center third of volume (0.108 in. diameter cylinder)	30-60,000
Middle third of volume (0.108 in. to 0.152 in. diam annulus)	60-90,000
Outer third of volume (0.152 to 0.191 in. diam annulus)	90-140,000

Similar calculations are in progress for the 17,000 and 34,000 MW-d/tonne (average) burnup specimens.

The calculations on the high burnup, high power, experiment also indicate that the irradiation may be performed in a single flux location. The previous plan called for movement of the capsule to successively higher flux locations, in order to keep the fuel temperature from decreasing beyond 10% of the design value. The change in the calculation results is due to the more realistic evaluation of the flux perturbation factor.

Mechanical design changes included the increase of gas space in the high burnup specimens, and a number of modifications to make assembly and disassembly of the experiments easier. The modifications were suggested by experience with the W1-1 capsule.

4.4 CONSTRUCTION OF UC-PuC EXPERIMENTS

The construction and receipt of components for the six UC-PuC capsules are complete with the exception of some of the specimen parts and delivery of individually calibrated thermocouples. The assembly and inspection of the instrument consoles were completed.

A device to load the specimens with fuel, without contaminating the outside of the cladding, was developed.

Assembly of the experiments will start as soon as fuel pellets of acceptable and reproducible character are made.

5. PLUTONIUM FACILITIES

Both the United Nuclear Corporation and The Carborundum Company pluto-
nium facilities operated satisfactorily, with only minor maintenance required. The
contamination level in both facilities is zero.

Final assembly of the high temperature measurement box and cooling system
was completed in White Plains. Shipment to and installation of the box in Pawling
was postponed until July 1962.

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