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STUDY OF URANIUM-PLUTONIUM MONOXIDES

Final Summary Report

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ABSTRACT

Uranium-plutonium monoxide compositions of the types $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ and $(U_{0.9}Pu_{0.1})(O_xC_yN_z)$ were synthesized by carbon and uranium reduction methods starting with UO_2 - PuO_2 mixtures. Pure $(UPu)O$ or PuO compounds, as well as nitrogen-stabilized uranium-plutonium monoxides $(U_{0.9}Pu_{0.1})(O_xN_{1-x})$, could not be synthesized. The maximum oxygen content found in essentially single-phase $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ was approximately $x = 0.4$. Higher monoxide oxygen contents, approaching $x = 0.6$, were found in materials containing 15% or more of a dioxide phase. Nearly single-phase $(U_{0.9}Pu_{0.1})(O_xC_yN_z)$ compositions were obtained when the intended oxygen content was no greater than $x = 0.3$ and the O/C atom ratio was no more than 1. $Pu(O_xC_{1-x})$ compositions were prepared having estimated oxygen contents as high as $x = 0.6$. Corrosion testing to evaluate these fuels for water-cooled thermal reactor application demonstrated that: (1) in boiling water, the $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ materials hydrolyzed while $(U_{0.9}Pu_{0.1})(O_xC_yN_z)$ compositions with carbon contents less than $y = 0.4$ were essentially unaffected; and (2) in 550°F water, all monoxide-type materials disintegrated. Typical monoxide-type compositions appeared to have higher room temperature thermal conductivities than those of $(UPu)O_2$ and UO_2 .

FOREWORD

The United States and the European Atomic Energy Community (Euratom), on May 29 and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U.S.-Euratom Research and Development Program which is aimed at reactors to be constructed under the Joint Program.

The work described in this report represents the Joint U.S.-Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

The study of uranium-plutonium monoxides was sponsored jointly by the USAEC and Euratom. The prime contractor was the United Nuclear Corporation, Research and Engineering Center, and the subcontractor was the Carborundum Company. United Nuclear conducted fabrication studies in vacuum and performed property determinations. Carborundum conducted fabrication studies in helium.

This final report summarizes the results of the development program from its initiation on February 1, 1964. Previous progress was reported in:

UNC-5096, Study of Uranium-Plutonium Monoxides, Progress Report, Period of February 1, 1964 through June 31, 1964 (Oct. 5, 1964).

UNC-5102, Study of Uranium-Plutonium Monoxides, Progress Report, Period of August 1, 1964 through October 31, 1964 (Dec. 28, 1964).

UNC-5117, Study of Uranium-Plutonium Monoxides, Progress Report, Period of November 1, 1964 through March 31, 1965 (Apr. 15, 1965).

UNC-5132, Study of Uranium-Plutonium Monoxides, Progress Report, Period of April 1, 1965 through June 30, 1965 (Sept. 15, 1965).

UNC-5138, Study of Uranium-Plutonium Monoxides, Progress Report, Period of July 1, 1965 through September 30, 1965 (Oct. 30, 1965).

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1. SUMMARY

Fabrication studies were conducted to synthesize uranium-plutonium monoxide-type materials for evaluation as fuels for water-cooled thermal reactors. Two synthesis routes were investigated: (1) reduction of the mixed dioxides (PuO_2 and UO_2) with carbon, and (2) reduction of the mixed dioxides with uranium metal. Both reactions were carried out in helium and in vacuum at temperatures ranging from 1450 to 1900°C.

Initially, it was found that a pure monoxide, $(\text{UPu})\text{O}$, could not be synthesized. Essentially single-phase $\text{M}(\text{O}_x\text{C}_{1-x})^*$ compositions could be prepared by carbon reduction in both helium and vacuum. The maximum oxygen content found was approximately $x = 0.4$. Similar products were obtained in the case of uranium metal reduction in helium, provided carbon in the form of UC or C was added to stabilize the monoxide structure; however, in vacuum this route led to an undesirable metal phase in the product.

Higher oxygen contents, approaching $x = 0.6$, were produced by the carbon reduction route; however, the monoxide weight fraction was limited to 60 w/o. Efforts to increase the oxygen content and the weight fraction of the monoxide-type phase by (1) crushing, repressing, and resintering, and (2) employing higher reaction temperatures were unsuccessful. The substitution of phenolformaldehyde for carbon powder as the reducing agent promised to increase the

* $\text{M} = \text{U}_{0.9}\text{Pu}_{0.1}$.

monoxide weight fraction significantly, but the maximum corresponding oxygen content remained at $x = 0.6$.

To obtain a superior water corrosion resistant material, the synthesis of $M(O_xC_yN_z)$ compositions was undertaken by uranium metal reduction of the mixed dioxides with UC and UN added, as well as by the carbon reduction method. Monoxide weight fractions of 90 w/o or greater were obtained when the intended oxygen content was no greater than $x = 0.3$ and the intended oxygen-to-carbon atom ratio was no more than 1.

Synthesis of a high oxygen substantially single-phase monoxide-type material stabilized with nitrogen, i.e., an $M(O_xN_{1-x})$ compound, did not appear possible as the oxygen solubility in the nitride phase was low.

Corrosion test specimens of the $M(O_xC_{1-x})$ compositions, having oxygen contents as high as $x = 0.37$, disintegrated within one hour in boiling water. Generally, $M(O_xC_yN_z)$ compositions containing carbon contents of $y < 0.4$ survived exposure to boiling water, while those containing $y > 0.4$ disintegrated in boiling water. All $M(O_xC_yN_z)$ materials tested in 550°F water disintegrated within an hour.

Thermal diffusivity measurements indicated that monoxide-type materials had higher room temperature thermal conductivities than $(UPu)O_2$ or UO_2 .

2. INTRODUCTION

The goal of this study was to find a uranium-plutonium monoxide-type fuel for water-cooled thermal reactors which would have a heat generation capability better than, and water corrosion resistance equivalent to, PuO_2 and $(\text{UPu})\text{O}_2$.

The expected higher density and higher thermal conductivity of monoxide-type fuels as compared with UO_2 provided the incentive for the investigation. Briefly, if these new fuels could be shown to have adequate corrosion resistance in the environment of a water-cooled reactor, it would be possible to achieve cost savings by specifying larger tolerances for fuel pellet diameter and cladding ID than are currently being used for UO_2 fuel rods or by utilizing fewer larger-diameter fuel rods. A possible performance advance might be made by operating the new fuels at a higher specific power.

Plutonium enrichment was employed in this study in anticipation of the day when sufficient plutonium would be available to reduce reliance on uranium isotope enrichment facilities. Although early core loadings would use Pu^{239} , subsequent ones could use increasing amounts of Pu^{240} to increase the reactivity burnup limit of the reactor. Total plutonium concentrations of up to 10% would be introduced into the uranium fuel.

Early interest in monoxide-type materials was generated by the reported existence of UO thin films having a NaCl structure with a lattice parameter of

4.92 ± 0.02 .¹ Based on similarity of its crystal structure to that of known high thermal conductivity monocarbide and mononitride, it was expected that the monoxide should also have a high thermal conductivity. When this study was initiated, however, it had been fairly well established that UO was not thermodynamically stable in massive form. For example, Vaughan et al.,² in attempting to prepare UO by reacting UC with UO_2 , produced $\text{U}(\text{O}_x\text{C}_{1-x})$ compositions with a maximum oxygen content of approximately $x = 0.5$. Other investigators, including Magnier et al.,³ Brett et al.,⁴ Stoops and Hamme⁵ and Sano et al.,⁶ subsequently determined the maximum replacement of carbon by oxygen in the UC structure. Similar data were also developed by Henry⁷ in his study of the UC-UO-UN system. Although the maximum oxygen solubilities reported by these workers ranged from $x = 0.25$ to $x = 0.84$, Henry⁷ concluded that a consideration of all of the data from these studies would indicate a solubility near $x = 0.35$.

As in the case of UO, the existence of PuO in the form of thin films was also reported.⁸ In addition, Westrum⁹ stated that PuO was prepared in 1944 by the barium reduction of PuOCl , and Dirksen⁹ found it in the product when PuO_2 was reduced with barium. Akimoto¹⁰ claimed to have synthesized PuO by the oxidation of plutonium with a stoichiometric amount of oxygen in a closed system. Although recent investigators have been unable to confirm the existence of PuO, several have produced a $\text{Pu}(\text{O}_x\text{C}_{1-x})$ -type analogous to the uranium monoxide-type discussed above. These include Skavdahl,¹¹ Brett et al.,⁴ and Mulford,¹² who reported a maximum oxygen content of about $x = 0.6$. Brett et al. also produced a $(\text{U}_{0.85}\text{Pu}_{0.15})(\text{O}_x\text{C}_{1-x})$ -type in which the maximum oxygen content was approximately $x = 0.5$. These materials were synthesized by reduction of a higher oxide in a system containing carbon. In some instances, depending upon the mixture reacted, CO was evolved. According to Brett et al., the maximum ratio of oxygen to carbon in the monoxide depends partially on the method of synthesis, the best results being obtained in a vacuum where the CO pressure is kept low.

The specific objectives of this study were: (1) to fabricate uranium-plutonium monoxide-type compositions with or without stabilizers, such as carbon and nitrogen; and (2) to measure pertinent properties of promising materials, particularly water corrosion resistance and thermal conductivity.

Two synthesis routes were studied: (1) reduction of the mixed dioxides (PuO_2 and UO_2) with carbon; and (2) reduction of the mixed dioxides by noncarbonaceous agents, such as uranium metal. The reactions were carried out in helium and in vacuum. The fuels were evaluated by metallography, chemical analysis, X-ray diffraction, and density measurements. Generally, a uranium-plutonium ratio of 9:1 was used to represent the maximum enrichment of plutonium-fueled thermal reactors.

3. FABRICATION STUDIES

3.1 EXPERIMENTAL METHODS

3.1.1 Starting Materials

The following starting materials were used to synthesize monoxide-type products in these fabrication studies: (1) depleted uranium dioxide, UO_2 ; (2) plutonium dioxide, PuO_2 ; (3) carbon, C; (4) uranium hydride, UH_x ; (5) uranium carbide, UC; and (6) uranium nitride, UN. Carbon and uranium hydride were employed to reduce the mixed dioxides in the carbon reduction and uranium metal reduction methods, respectively, the hydride being the precursor of the metal. Uranium carbide and/or uranium nitride was added to the reaction mixtures in the metal reduction experiments to provide carbon and/or nitrogen stabilizer in the monoxide-type products. Chemical and spectrographic analytical data as well as other pertinent properties of these starting materials are presented in the Appendix.

3.1.2 Synthesis Procedures

The synthesis process operations preceding the heating step, consisted of weighing, blending, and compacting. These were performed in a dry helium atmosphere containing less than 80 ppm water and less than 100 ppm of oxygen. The starting materials were weighed on either a torsion or an analytical balance. Reaction mixtures were blended in a rubber-lined ball mill with stainless steel

balls, or in a Spex mill (a commercial oscillating shaker*). The blended materials were usually compacted into 1/4-in. diameter pellets with a manually operated hydraulic press, at various compacting pressures, using dies of hardened alloy steel.

For helium atmosphere synthesis, heating of the compacts in a tantalum container was performed in a graphite resistance-heated furnace through which helium flowed at 6 ft³/hr, in the case of the uranium metal reductions, and 30 ft³/hr, in the case of the carbon reductions. The helium, containing <7 ppm oxygen, was taken from the glove box atmosphere and passed through a drying column to reduce moisture content to <15 ppm before entering the furnace.

For vacuum synthesis, the compacts were contained in an open tantalum crucible and heated in a tantalum resistance-heated furnace. A pressure of less than 1-micron Hg was maintained during the synthesis run.

3.1.3 Characterization Procedures

The reaction products were usually characterized by (1) chemical analysis for carbon and nitrogen, (2) X-ray analysis to identify the phases present, (3) metallography and point counting to determine the amount of each phase present, and (4) density measurements. The various analytical and metallographic procedures employed are described in the Appendix. X-ray analysis was performed on powder samples by a standard diffraction technique. Specimen densities were determined by calculation from weights and dimensions or by a gravimetric displacement method using carbon tetrachloride.

The weight fractions of the phases found in the products were calculated from volume fraction data obtained from point counting and from phase densities based on X-ray data. The carbon and/or nitrogen content reported for the mon-

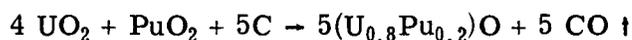
*Made by Spex Industries, Model 5000 (3-ml capacity) and Model 8000 (25-ml capacity).

oxide-type phase was calculated by assuming all the carbon and/or nitrogen found in the product by chemical analysis was in that phase. The oxygen content of the monoxide-type phase was then determined by difference, assuming that the ratio of metal atoms to atoms of oxygen plus carbon and/or nitrogen was equal to unity.

3.2 SYNTHESIS OF $(UPu)(O_xC_{1-x})$ COMPOSITIONS

3.2.1 Intended $(UPu)O$

At the outset, two series of preliminary experiments were conducted to establish whether the $(UPu)O$ in bulk form could be synthesized. In one series, a carbon reduction of the mixed dioxides to produce intended $(U_{0.8}Pu_{0.2})O$ was attempted in accordance with the following reaction:



A stoichiometric mixture of the starting materials was blended, compacted, and reacted in helium at several temperatures in the 1650 to 2000°C range. The results of X-ray analysis, shown in Table 1, indicate that every product contained an oxygen deficient dioxide phase and a monoxide-type phase. The finding of 1 w/o residual carbon in the product, in conjunction with metallographic evidence showing only the two phase types present, supported the conclusion that the monoxide-type was a $(UPu)(O_xC_{1-x})$ composition. In addition, the monoxide phase etched differently from pure carbide and its lattice parameter was significantly lower than that of monocarbide.

In the second series of experiments, the feasibility of synthesizing a monoxide by uranium metal reduction of PuO_2 was investigated by conducting the following intended reaction employing UH_x as a source of uranium metal:

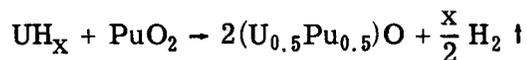


TABLE 1 — SYNTHESIS OF INTENDED $(U_{0.8}Pu_{0.2})O$ BY CARBON REDUCTION OF UO_2 AND PuO_2 IN HELIUM

Exp. No.	Temp, °C (Hold Time, hr)	Carbon Content of Product, w/o	X-Ray Analysis (Phase Intensity, and Lattice Parameter, Å)		
			Dioxide-Type	Monoxide-Type	(UPu)C ₂ -Type
1	1650 (5)	1.09	Major, two phases $a_1 = 5.482 \pm 0.002$ $a_2 = 5.4732 \pm 0.0009$	Moderate/strong $a = 4.9565 \pm 0.0002$	Indication
2	1760 (6)	0.96	Major, three phases $a_1 = 5.4938 \pm 0.0007$ $a_2 = 5.4841 \pm 0.0009$ $a_3 = 5.475 \pm 0.001$	Moderate $a = 4.9540 \pm 0.0007$	Not detected
3	1850 (3½)	0.98	Major, two phases $a_1 = 5.4959 \pm 0.0009$ $a_2 = 5.4864 \pm 0.0003$	Weak $a = 4.945 \pm 0.003$	Not detected
4	1850 (4) Product crushed, pressed, reheated to 1850 (2)	1.07	Major $a = 5.4908 \pm 0.0005$	Moderate $a = 4.9456 \pm 0.0006$	Not detected
5	Product from Exp.4 crushed, pressed, and reheated to 2000 (1)	0.90	Major, several phases* $a = 5.4929 \pm 0.0006$ (avg)	Moderate/strong,* several phases $a = 4.9429 \pm 0.0007$ (avg)	Not detected

*Metallography indicated an approximate mixture of 50 v/o dioxide and 50 v/o monoxide-type.

The only carbon introduced was that present as an impurity in the starting materials, approximately 0.06 w/o. The reaction mixture was compacted and heated under helium in sealed tantalum containers to synthesis temperatures ranging from 1200 to 1800°C. The results of product characterization presented in Table 2 indicate that no monoxide-type phase was detected except in two cases where traces were found. It is believed that these were $(UPu)(O_xC_{1-x})$ compositions containing carbon derived from the starting material impurities.

Based on the results of these two sets of preliminary experiments, it was concluded that a pure monoxide could not be made and that carbon was necessary to stabilize the hypothetical $(UPu)O$ phase.

3.2.2 Intended $(UPu)(O_xC_{1-x})$ by Uranium Metal Reduction

Helium Atmosphere Experiments

A. Preliminary Syntheses

The apparent need for carbon as a monoxide stabilizer prompted an investigation of a uranium metal reduction method in which carbon in the form of UC was added to the reaction mixture. The principal objectives, initially, were (1) to establish the conditions for synthesizing single-phase $(UPu)(O_xC_{1-x})$ materials, and (2) to determine the composition of the carbon-stabilized monoxides produced.

This synthesis method had the following potential advantages over the carbon reduction route, which was also under study. It appeared that reaction sintering, i.e., concurrent synthesis and densification, could be promoted by the use of the low melting uranium metal. Ideally, no CO was produced which would require removal to complete the reaction. A UO_2 -type surface layer, usually obtained in carbon reduction, did not form.

TABLE 2 — SYNTHESIS OF INTENDED $(U_{0.5}Pu_{0.5})O$ BY URANIUM METAL REDUCTION OF PuO_2

Exp. No.	Temp, °C (Hold Time, hr)	Carbon Content of Product, w/o	X-Ray Analysis* (Phase Intensity, and Lattice Parameter, Å)		
			Dioxide-Type	Monoxide-Type	β Pu_2O_3
1	1200 (1)	0.030	Major, two phases $a_1 = 5.518 \pm 0.002$ $a_2 = 5.469 \pm 0.003$	Weak	Weak
2	1400 (1)	0.053	Major $a = 5.518 \pm 0.001$	—	Indication
3	1600 (1)	0.051	Major $a = 5.5191 \pm 0.0002$	Indication	—
4	1800 (1)	0.040	Major $a = 5.5163 \pm 0.0006$	—	—

*An unidentified phase was detected in all of these experiments.

In the initial experiments, five different intended reactions were conducted to produce five nominal $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ compositions with x values ranging from 0.2 to 1.0. In each case, the reaction mixture was stoichiometrically formulated on the basis of the intended reaction. A typical reaction, that for $x = 0.4$, is as follows:



The finely divided starting materials were blended in a 25-ml Spex mixer, and, after addition of Carbowax-6000 binder, the blend was compacted into pellets at 30,000 psi. (Conventional ball milling techniques were not applicable because the reactants, particularly the uranium hydride, adhered tenaciously to the steel grinding balls.) The pellets were then heated to the synthesis temperature of 1650°C and held for 5 hr in helium flowing at 6 ft³/hr. The synthesis products were characterized in the usual manner by metallography, point count, X-ray diffraction analysis, carbon analysis, and density measurement. The amount of each phase and the $M(O_xC_{1-x})$ composition were calculated by the procedure described in Section 3.1.3. The results summarized in Table 3 under the "a" series indicate that a maximum monoxide oxygen content of $x = 0.51$ was found in the products of the intended MO synthesis. However, the monoxide weight fraction present was only 6 w/o. (Carbon to stabilize the monoxide phase was probably derived from the graphite furnace during synthesis and/or from impurities in the starting materials.) The identification of a metal phase in Experiments 1a, 2a, and 3a was based on response to bromine etching. X-ray diffraction analysis confirmed the presence of metal in the case of Experiment 1a. It is noteworthy that nearly single-phase $M(O_xC_{1-x})$ was produced when the intended oxygen content was $x \leq 0.4$. A photomicrograph of one of these materials is shown in Fig. 1.

TABLE 3 — SYNTHESIS OF $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ BY URANIUM METAL REDUCTION AT 1650°C IN HELIUM AND EFFECT OF ANNEALING AT 1200°C

Exp. * No.	Intended Composition	Calculated† $M(O_xC_{1-x})$ Composition	Carbon Content of Product, w/o	Pellet Density, g/cm ³	Phase Content, w/o			X-Ray Diffraction Analysis (Lattice Parameter, Å)	
					$M(O_xC_{1-x})$	MO ₂	Metal	$M(O_xC_{1-x})$	MO ₂ -Type
1a	MO‡	$M(O_{0.51}C_{0.49})$	0.14	10.6	6	47	47	§	5.4825 ± 0.0002
1b		$M(O_{0.58}C_{0.42})$	0.14	10.8	7	41	52	§	5.4810 ± 0.0006
2a	$M(O_{0.8}C_{0.2})$	$M(O_{0.47}C_{0.53})$	1.06	11.3	42	41	17	4.9482 ± 0.0003	5.4839 ± 0.0010
2b		$M(O_{0.58}C_{0.42})$	1.09	—	55	27	18	4.9478 ± 0.0001	5.4850 ± 0.0010
3a	$M(O_{0.6}C_{0.4})$	$M(O_{0.41}C_{0.59})$	2.04	11.3	72	19	10	4.9491 ± 0.0003	5.4876 ± 0.0010
3b		$M(O_{0.42}C_{0.58})$	1.93	11.4	69	26	6	4.9490 ± 0.0006	5.4886 ± 0.0008
4a	$M(O_{0.4}C_{0.6})$	$M(O_{0.34}C_{0.66})$	2.93	12.6	93	7	—	4.9542 ± 0.0008	5.486
4b		$M(O_{0.35}C_{0.65})$	2.88	12.7	93	7	—	4.9537 ± 0.0002	—
5a	$M(O_{0.2}C_{0.8})$	$M(O_{0.18}C_{0.82})$	3.79	11.3	96	4	—	4.9609 ± 0.0002	5.473
5b		$M(O_{0.21}C_{0.79})$	3.70	11.2	98	2	—	4.9600 ± 0.0001	—

*a series = synthesis at 1650°C, 5 hr; b series = annealing of synthesis products at 1200°C, 5 hr.

†Composition was calculated from point count, carbon content, and X-ray density.

‡M = $(U_{0.9}Pu_{0.1})$.

§Weak $M(O_xC_{1-x})$ pattern, uranium metal also detected.

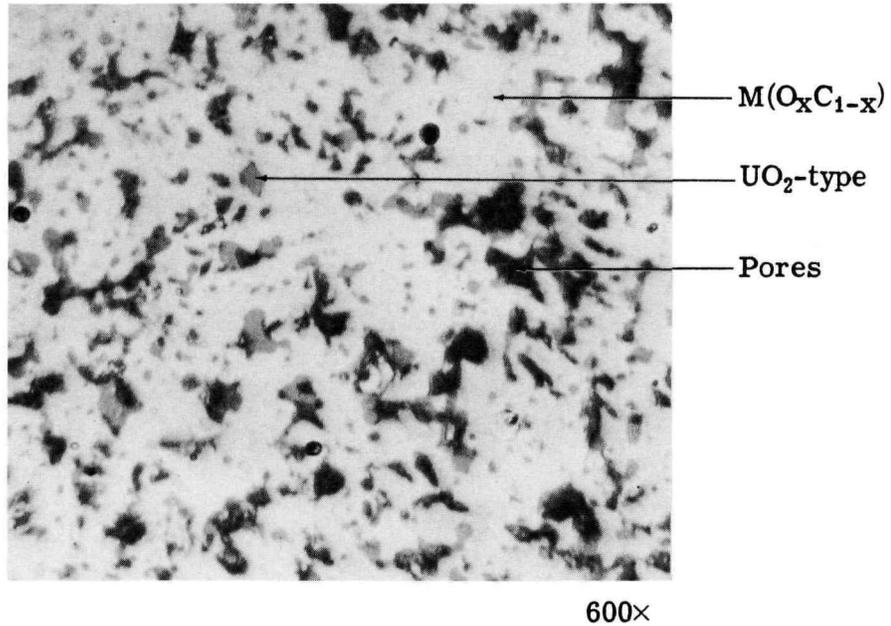


Fig. 1 — Intended (U_{0.9}Pu_{0.1})(O_{0.4}C_{0.6}) Synthesized by Uranium Metal Reduction in Helium

Synthesized in helium by the uranium metal reduction of UO₂ and PuO₂ with UC at 1650°C, 5 hr
(Table 3, Experiment 4a)

Total carbon:	2.93 w/o
X-ray analysis:	Major M(O _x C _{1-x}) Weak/moderate UO ₂ -type
M(O _x C _{1-x}) phase:	93 w/o
Composition:	M(O _{0.34} C _{0.66})

B. Effect of Annealing

Representative products from the five synthesis experiments were annealed at 1200°C for 5 hr to determine the effect on amount, composition, and lattice parameter of the $M(O_xC_{1-x})$ phase. The results of annealed product characterization are included in Table 3 to permit comparison with the as-synthesized products. The phases identified by X-ray diffraction and metallography were the same as before the low temperature anneal. Except in the case of Experiment 2, the $M(O_xC_{1-x})$ weight fraction was virtually unchanged. Generally, the oxygen content, x , was increased by the annealing treatment.

The variation of $M(O_xC_{1-x})$ lattice parameter with oxygen content is shown in Fig. 2. A uniform decrease in lattice parameter was observed as x increased. There appeared to be a definite change in the shape of the curve at about $x = 0.4$. However, this did not appear to be indicative of the maximum oxygen possible in $M(O_xC_{1-x})$ since compositions having $x = 0.58$ were found by the point count method. Annealing at 1200°C did not significantly affect the lattice parameter-oxygen content relationship. A possible interpretation of this finding is that there was little difference in the amount of metal dissolved in the $M(O_xC_{1-x})$ phase before and after annealing.

C. Effect of Process Variations

To maximize the weight fraction and the oxygen content of the $M(O_xC_{1-x})$ phase, two synthesis studies (each involving a different intended composition), were conducted involving variations of blending conditions and reaction hold time at 1650°C.

In the first study, the reactants UO_2 , PuO_2 , UH_x , and UC were batched in stoichiometric proportions to produce $M(O_{0.4}C_{0.6})$, and were blended in a 25-ml capacity Spex mixer for periods of 15, 30, and 60 minutes. Compacts were cold pressed from each blend without binder at 30,000 psi. Synthesis hold times of 1.5, 3.5, and 5 hr at 1650°C were investigated.

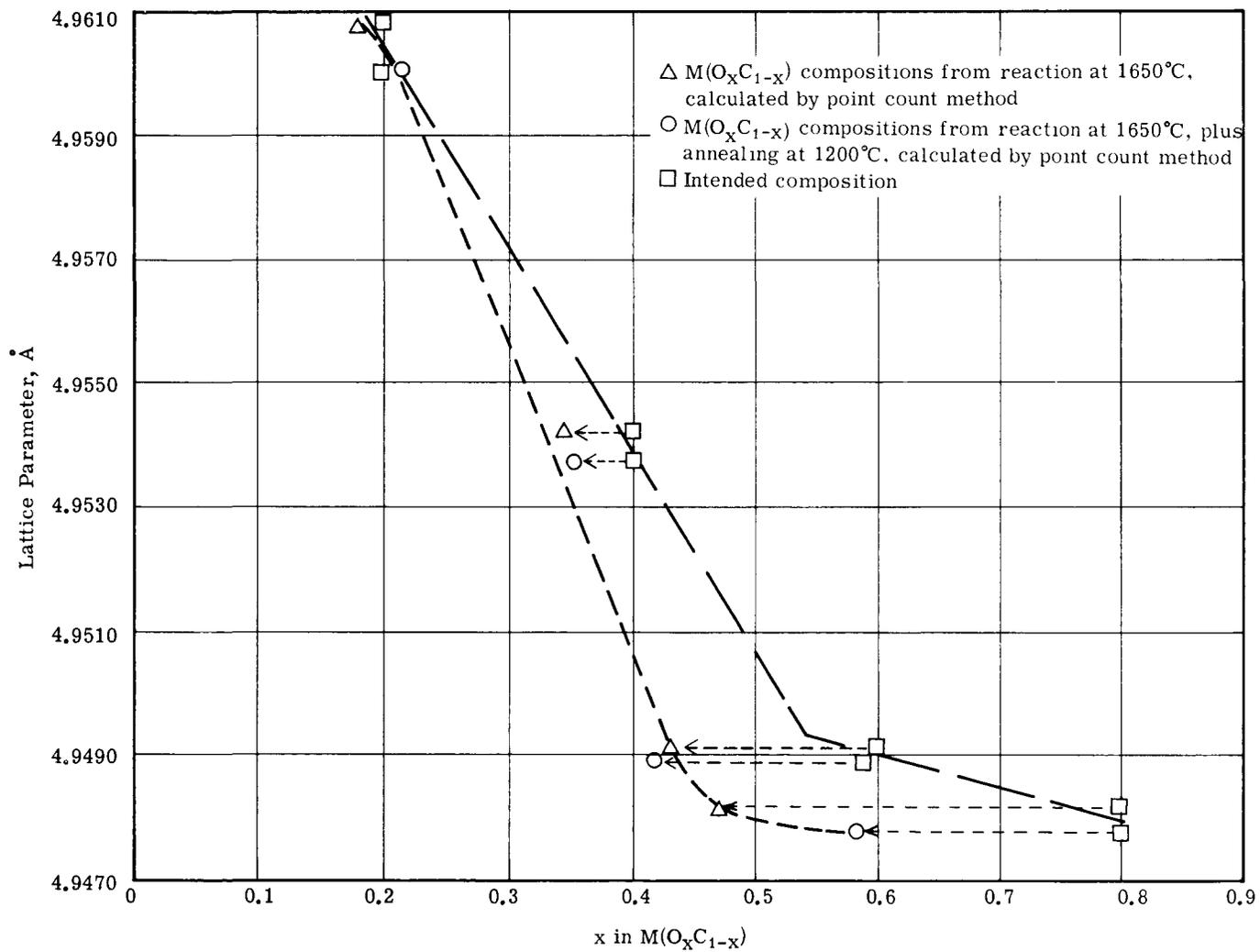


Fig. 2 — Variation of $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ Lattice Parameter with Oxygen Content
 Reaction of U, UO_2 , PuO_2 , and UC in Helium

The results of this set of synthesis runs are presented in Table 4 and the significant findings are as follows.

1. Metallographic examination indicated only two phases were present, $M(O_xC_{1-x})$ and a dioxide-type.
2. Phase equilibrium was reached after 1.5 hr for the 60-minute blended materials. The maximum pellet density was achieved with the 5-hr hold time.
3. Blending time variations had little effect on $M(O_xC_{1-x})$ composition as indicated by lattice parameter and calculated composition data.
4. The maximum $M(O_xC_{1-x})$ weight fraction was 95 w/o corresponding to a 30-minute blending time.
5. The highest value of x found in the product of the intended $M(O_{0.4}C_{0.6})$ synthesis was 0.34.

In an attempt to produce $M(O_xC_{1-x})$ compositions with higher oxygen contents, a second synthesis study was conducted in which the intended composition was $M(O_{0.6}C_{0.4})$. The reactants were Spex-blended for 30 minutes and compacted at 30,000 psi.

Synthesis hold times of 1.5 and 3.5 hr at 1650°C were investigated. In addition, the effect on composition of a programmed heat treatment of 2 hr at 1100°C, 1 hr at 1400°C, and 5 hr at 1650°C was examined.

The results shown in Table 5 indicate that equilibrium conditions were reached in 1.5 hr or less at 1650°C. This was confirmed by metallographic examination which showed that the calculated $M(O_{0.36}C_{0.64})$ phase was in intimate contact with an oxygen deficient dioxide phase and free metal (as illustrated in Fig. 3). These results are in substantial agreement with those of the preliminary syntheses of intended $M(O_{0.6}C_{0.4})$ from which free metal was also obtained (see Table 3). In this earlier work, higher intended oxygen contents produced more metal phase

TABLE 4 — EFFECT OF BLENDING TIME AND HOLD TIME — INTENDED $(U_{0.9}Pu_{0.1})(O_{0.4}C_{0.6})$ PREPARED BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC IN HELIUM

Exp. No.	Spex Blending Time, minutes	Hold Time at 1650°C, hr	Carbon Content in Product, w/o	Amount of $M(O_xC_{1-x})$ Phase, w/o	Calculated $M(O_xC_{1-x})$ Composition*	X-Ray Diffraction Analysis		Pellet Density, g/cm ³
						Phase Intensity	Lattice Parameter, Å	
1	60	1½	2.91	91	$M(O_{0.33}C_{0.67})$ †	Major $M(O_xC_{1-x})$ Moderate MO_{2-x}	4.9535 ± 0.0011	12.6
2	60	3½	2.92	89	$M(O_{0.32}C_{0.68})$	Major $M(O_xC_{1-x})$ Moderate MO_{2-x}	4.9540 ± 0.0005	12.7
3‡	60	5	2.97	91	$M(O_{0.32}C_{0.68})$	Major $M(O_xC_{1-x})$ Weak/mod. MO_{2-x}	4.9543 ± 0.0005	12.9
4	30	5	3.00	95	$M(O_{0.34}C_{0.66})$	Major $M(O_xC_{1-x})$ Weak/mod. MO_{2-x}	4.9537 ± 0.0015	12.7
5	15	5	2.93	93	$M(O_{0.34}C_{0.66})$	Major $M(O_xC_{1-x})$ Weak/mod. MO_{2-x}	4.9542 ± 0.0008	12.6

*Composition was calculated from X-ray density, point count, and carbon content.

† $M = (U_{0.9}Pu_{0.1})$.

‡Specimens from Exp. 2 reheated an additional 1½ hr.

TABLE 5 — EFFECT OF HOLD TIME — INTENDED ($U_{0.9}Pu_{0.1}$)($O_{0.6}C_{0.4}$) BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC IN HELIUM

Exp. No.	Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Phase Content by Point Count, w/o			Calculated $M(O_xC_{1-x})$ Composition*	X-Ray Diffraction Analysis		Pellet Density, g/cm^3
			$M(O_xC_{1-x})$	MO_2	Metal		Phase Intensity	Lattice Parameter, Å	
1	1100 (2) + 1400 (1) + 1650 (1½)	2.00	66	26	18	$M(O_{0.36}C_{0.64})^\dagger$	Major $M(O_xC_{1-x})$ Strong MO_{2-x}	4.9493 ± 0.0009 Not determined	12.5
2	1650 (1½)	2.05	67	22	12	$M(O_{0.36}C_{0.64})$	Major MO_{2-x} Strong $M(O_xC_{1-x})$ Faint/weak βPu_2O_3	5.4900 ± 0.0005 4.9492 ± 0.0009	12.5
3	1650 (3½)	2.01	66	23	11	$M(O_{0.36}C_{0.64})$	Major $M(O_xC_{1-x})$ Strong MO_{2-x}	4.9498 ± 0.0005 5.4894 ± 0.0008	12.5

*Composition was calculated from X-ray density, point count, and carbon content.

† $M = (U_{0.9}Pu_{0.1})$.

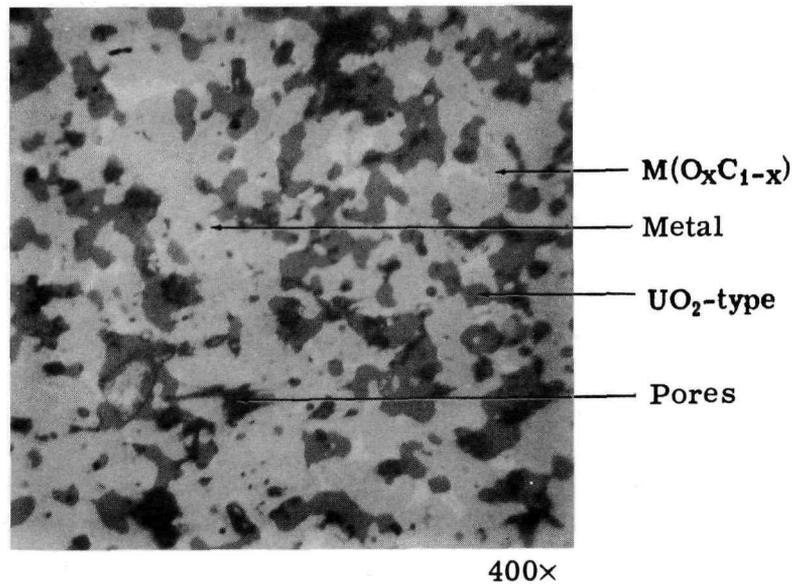


Fig. 3 — Intended $(U_{0.9}Pu_{0.1})(O_{0.6}C_{0.4})$ Synthesized by Uranium Metal Reduction in Helium — 3.5 hr at $1650^{\circ}C$

Effect of hold time on the synthesis in helium by uranium metal reduction of UO_2 and PuO_2 with UC at $1650^{\circ}C$, 3.5 hr

(Table 5, Experiment 3)

Total carbon:	2.01 w/o
X-ray analysis:	Major $M(O_x C_{1-x})$ Strong MO_{2-x}
$M(O_x C_{1-x})$ phase:	66 w/o
Composition:	$M(O_{0.36}C_{0.64})$

as well as a lower $M(O_xC_{1-x})$ weight fraction. It appears, therefore, that the uranium metal reduction in helium is not capable of producing essentially single-phase monoxide-type compositions with oxygen contents greater than approximately $x = 0.4$.

Vacuum Experiments

Synthesis by uranium metal reduction in vacuum instead of in helium was also investigated to determine the effect on amount and composition of the $M(O_xC_{1-x})$ phase produced. In one set of experiments the carbon stabilizer was introduced as free carbon, while in another set UC was employed. The intended oxygen contents ranged from $x = 1.0$ to 0.2 . Syntheses were conducted at 1650 and 1750°C , and hold times were varied from 0.5 to 5 hr.

The starting materials, either UH_x , C, UO_2 and PuO_2 or UH_x , UC, UO_2 and PuO_2 , were blended in a Spex mixer, compacted, and reacted in a vacuum furnace. The results of product characterization are presented in Tables 6 and 7 for the two reaction mixture types, respectively.

In the case of uranium metal reduction with free carbon added, the products after 2 hr at 1650°C were found to be porous, and it was not believed that phase equilibrium had been reached. Although some densification occurred after an additional 3 hr at 1650°C , the data in Table 6 indicate that metal was present in every case and either the $M(O_xC_{1-x})$ weight fraction or oxygen content was relatively low. Table 6 also includes the results of a 1750°C synthesis of intended $M(O_{0.4}C_{0.6})$ by the same reduction method employing two hold times, 0.5 and 3 hr. Again, metal phase was present in the product and the oxygen content in $M(O_xC_{1-x})$ remained low.

Similar results were obtained for the uranium metal reductions with UC added as shown in Table 7. Invariably, metal was present and the products either exhibited low $M(O_xC_{1-x})$ weight fractions or low x values.

TABLE 6 — SYNTHESIS OF $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ COMPOSITIONS BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH CARBON IN VACUUM

Exp. No.	Intended Composition	Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Amount of $M(O_xC_{1-x})$ Phase, w/o	Calculated Composition *	Phases Present by Metallography
1	$M(O_{0.8}C_{0.2})$ †	1650 (2)	0.72	10	‡	UO_2 -type, metal, $M(O_xC_{1-x})$
2	$M(O_{0.6}C_{0.4})$	1650 (2)	1.87	48	$M(O_{0.18}C_{0.82})$	$M(O_xC_{1-x})$, UO_2 -type, metal
3	$M(O_{0.4}C_{0.6})$	1650 (2)	2.72	94	$M(O_{0.38}C_{0.62})$	$M(O_xC_{1-x})$, UO_2 -type
4	$M(O_{0.8}C_{0.2})$	1650 (5)	0.19	40	—	$M(O_xC_{1-x})$, UO_2 -type, metal
5	$M(O_{0.7}C_{0.3})$	1650 (5)	0.78	23	$M(O_{0.60}C_{0.40})$	$M(O_xC_{1-x})$, UO_2 -type, metal
6	$M(O_{0.6}C_{0.4})$	1650 (5)	1.40	40	$M(O_{0.45}C_{0.55})$	$M(O_xC_{1-x})$, UO_2 -type, metal
7	$M(O_{0.5}C_{0.5})$	1650 (5)	1.76	41	‡	$M(O_xC_{1-x})$, UO_2 -type, metal
8	$M(O_{0.4}C_{0.6})$	1650 (5)	2.35	64	$M(O_{0.22}C_{0.78})$	$M(O_xC_{1-x})$, UO_2 -type, metal
9	$M(O_{0.4}C_{0.6})$	1750 (1/2)	2.60	72	$M(O_{0.26}C_{0.74})$	$M(O_xC_{1-x})$, UO_2 -type, metal
10	$M(O_{0.4}C_{0.6})$	1750 (3)	2.35	61	$M(O_{0.19}C_{0.81})$	$M(O_xC_{1-x})$, UO_2 -type, metal

*Composition was calculated from point count, carbon content, and assumed X ray density.

†M = $(U_{0.9}Pu_{0.1})$.

‡Composition uncertain because of low carbon content and/or low $M(O_xC_{1-x})$ phase content.

TABLE 7 — SYNTHESIS OF $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ COMPOSITIONS BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC IN VACUUM

Exp. No.	Intended Composition	Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Amount of $M(O_xC_{1-x})$ Phase, w/o	Calculated $M(O_xC_{1-x})$ Composition*	Phases Present by Metallography
1	MO†	1650 (2)	0.03	2	‡	UO_2 -type, metal, trace $M(O_xC_{1-x})$
2	$M(O_{0.9}C_{0.1})$	1650 (2)	0.38	26	‡	$M(O_xC_{1-x})$, UO_2 -type, metal
3	$M(O_{0.8}C_{0.2})$	1650 (2)	0.71	34	$M(O_{0.56}C_{0.44})$	$M(O_xC_{1-x})$, UO_2 -type, metal
4	$M(O_{0.5}C_{0.5})$	1650 (2)	2.42	70	$M(O_{0.27}C_{0.73})$	$M(O_xC_{1-x})$, UO_2 -type, metal
5	$M(O_{0.4}C_{0.6})$	1650 (2)	2.83	90	$M(O_{0.34}C_{0.66})$	$M(O_xC_{1-x})$, UO_2 -type
6	MO	1650 (5)	0.06	4	‡	UO_2 -type, metal, $M(O_xC_{1-x})$
7	$M(O_{0.9}C_{0.1})$	1650 (5)	0.07	6	‡	UO_2 -type, metal, $M(O_xC_{1-x})$
8	$M(O_{0.8}C_{0.2})$	1650 (5)	0.25	5	‡	UO_2 -type, metal, $M(O_xC_{1-x})$
9	$M(O_{0.6}C_{0.4})$	1650 (5)	1.32	9	‡	UO_2 -type, metal, $M(O_xC_{1-x})$
10	$M(O_{0.5}C_{0.5})$	1650 (5)	2.26	43	$M(O_{0.35}C_{0.65})$	$M(O_xC_{1-x})$, UO_2 -type, metal
11	$M(O_{0.4}C_{0.6})$	1650 (5)	2.83	93	$M(O_{0.29}C_{0.71})$	$M(O_xC_{1-x})$, UO_2 -type, metal
12	$M(O_{0.2}C_{0.8})$	1650 (5)	3.52	89	$M(O_{0.17}C_{0.83})$	$M(O_xC_{1-x})$, UO_2 -type, metal
13	$M(O_{0.58}C_{0.42})$	1750 (1/2)	1.74	54	$M(O_{0.31}C_{0.69})$	$M(O_xC_{1-x})$, UO_2 -type, metal
14	$M(O_{0.4}C_{0.6})$	1750 (1/2)	2.67	65	$M(O_{0.13}C_{0.87})$	$M(O_xC_{1-x})$, UO_2 -type

*Composition was calculated from point count, carbon content, and assumed X-ray density.

†M = $(U_{0.9}Pu_{0.1})$.

‡Composition uncertain because of low carbon content and or low $M(O_xC_{1-x})$ phase content.

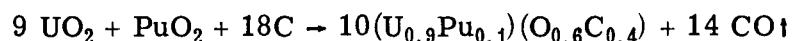
Clearly, uranium metal reduction in vacuum or in helium does not produce a promising monoxide-type material from the standpoint of single-phase $M(O_xC_{1-x})$ with oxygen contents greater than $x = 0.4$. In addition, the metal phase almost invariably present might lead to swelling as well as poor water corrosion resistance under reactor operating conditions. On the basis of these results, work was discontinued on this approach in favor of the carbon reduction method.

3.2.3 Intended (UPu)(O_xC_{1-x}) by Carbon Reduction

Helium Atmosphere Experiments

A. Preliminary Syntheses

The initial study of $M(O_xC_{1-x})$ synthesis by carbon reduction of UO_2 and PuO_2 was conducted with the objective of determining (1) the maximum oxygen content possible in the $M(O_xC_{1-x})$ phase, and (2) the conditions for producing a single-phase material. Four intended compositions with oxygen contents ranging from $x = 0.27$ to 0.60 were prepared. A typical intended reaction is as follows:



The starting materials were blended in stoichiometric quantities for 1/2 hr in a 25-ml Spex mixer. Binder (1/4 w/o Carbowax-6000 dissolved in benzene) was added, and the pellets were cold formed at 5000 psi. Synthesis was carried out by heating the compacts to 1650°C for 5 hr in a tantalum-lined graphite reaction crucible. A helium flow rate of 30 ft³/hr was maintained through the reaction crucible to carry away the gaseous binder and CO. The results of these preliminary experiments are presented in Table 8. Typical microstructures obtained are shown in Figs. 4 and 5.

TABLE 8 — SYNTHESIS OF INTENDED $(U_{0.9}Pu_{0.1})O$ AND $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ BY CARBON REDUCTION OF UO_2 AND PuO_2 IN HELIUM AT 1650°C FOR 5 HR

Exp. No.	Intended Composition	Calculated $M(O_xC_{1-x})$ Composition*	Carbon Content in Product, w/o	Phases by Metallography	Porosity by Point Count, v/o	Amount of $M(O_xC_{1-x})$ Phase, w/o	X-Ray Diffraction Analysis (Phase Intensity, Lattice Parameter, Å)	
							$M(O_xC_{1-x})$ Phase	UO_2 -Type Phase
1	MO	$M(O_{0.58}C_{0.42})$	1.18	$M(O_xC_{1-x})$ UO_2 -type (0.010-in. skin)	15	59	Moderate 4.9571 ± 0.0016 (Two phases) 4.9484 ± 0.0014	Strong 5.4794 ± 0.0010
2†	MO	$M(O_{0.58}C_{0.42})$	1.16	—	—	59	Moderate 4.9548 ± 0.0009	Strong 5.4795 ± 0.0002
3	$M(O_{0.6}C_{0.4})$	$M(O_{0.32}C_{0.68})$	2.51	$M(O_xC_{1-x})$ UO_2 -type (0.003-in. skin)	20	77	Strong 4.9576 ± 0.0006	Strong 5.4762 ± 0.0019
4	$M(O_{0.4}C_{0.6})$	$M(O_{0.28}C_{0.72})$	3.15	$M(O_xC_{1-x})$ UO_2 -type (0.0005-in. skin)	19	92	Major 4.9569 ± 0.0004	Very weak pattern in back reflection area
5	$M(O_{0.27}C_{0.73})$	$M(O_{0.25}C_{0.75})$	3.40	$M(O_xC_{1-x})$ UO_2 -type (No skin effect)	35	95	Major 4.9571 ± 0.0004	Very weak pattern in back reflection area

*The composition was calculated from X-ray data, point count, and carbon content.

†Heat treated at 1750°C for 4 hr.

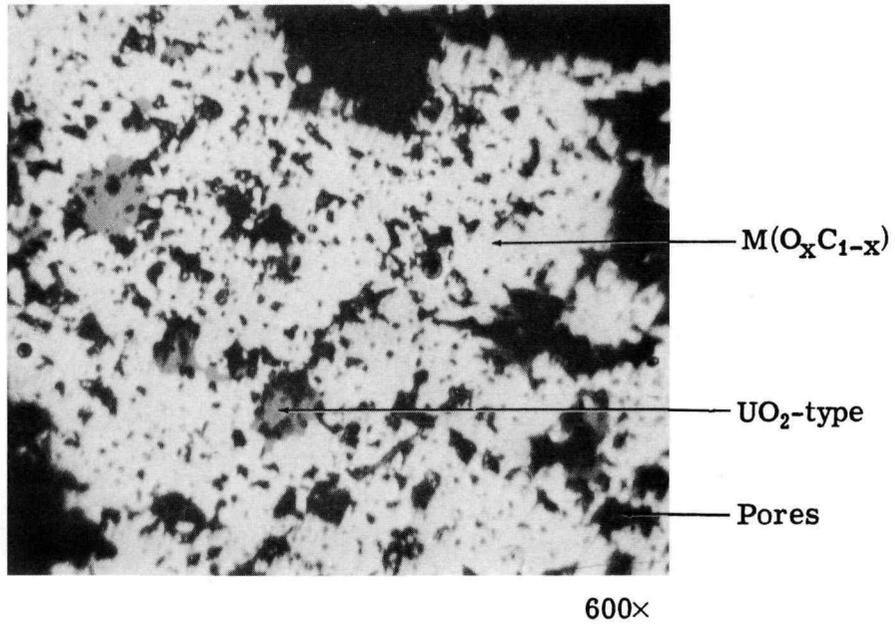


Fig. 4 — Intended $(U_{0.9}Pu_{0.1})(O_{0.27}C_{0.73})$ Synthesized by Carbon Reduction in Helium

Synthesized in helium from the carbon reduction of UO_2 and PuO_2 at $1650^\circ C$, 5 hr
(Table 8, Experiment 5)

Total carbon:	3.40 w/o
X-ray:	Major $M(O_xC_{1-x})$ Weak UO_2 -type
$M(O_xC_{1-x})$ phase:	95 w/o
Composition:	$M(O_{0.25}C_{0.75})$

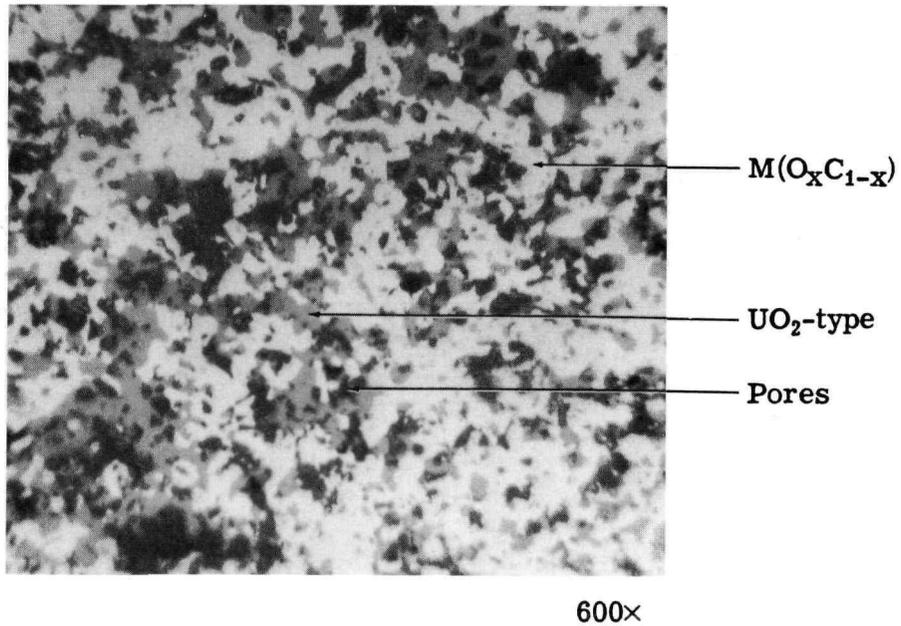


Fig. 5 — Intended (U_{0.9}Pu_{0.1})O Synthesized by Carbon Reduction in Helium

Synthesized in helium from the carbon reduction of
 UO₂ and PuO₂ at 1650°C, 5 hr
 (Table 8, Experiment 1)

Total carbon:	1.18 w/o
X-ray:	Moderate M(O _x C _{1-x}) Strong UO ₂ -type
M(O _x C _{1-x}) phase:	59 w/o
Composition:	(U _{0.9} Pu _{0.1})(O _{0.58} C _{0.42})

It is noteworthy that the highest content of $x = 0.58$ was obtained from an intended MO synthesis. However, the synthesis product contained only 59 w/o of the monoxide phase. As the intended oxygen content was decreased, the product became more nearly single phase with the actual oxygen content approaching the intended value. The maximum oxygen content found here is in good agreement with that obtained by the uranium metal reduction method.

As noted in Table 8, a thin layer of a UO_2 -type phase was found on the surface of most of the synthesis products during metallographic examination. The thickness of the layer, ranging to 10 mils, increased with increasing intended oxygen content. No such skin effect was observed in the case of intended $\text{M}(\text{O}_{0.27}\text{C}_{0.73})$.

Other investigators¹¹ have found a similar surface layer on the reaction product of PuO_2 and carbon, and have attributed it to vaporization of the monoxide-type phase from the surface of the pellet. However, in the present case, this explanation is not supported because of the following observations:

1. The surface layer did not develop in syntheses where the carbon content was relatively high.
2. The layer did not develop in any synthesis by uranium metal reduction in helium or in vacuum.
3. Materials containing the $\text{M}(\text{O}_x\text{C}_{1-x})$ phase were heated for several hours at temperatures as high as 1750°C without significant weight change.

B. Effect of Reheating

Carbon stabilized monoxide compositions having intended oxygen contents of $x = 0.27, 0.40,$ and 0.60 were subjected to various crushing and reheating steps to determine the effect on $\text{M}(\text{O}_x\text{C}_{1-x})$ weight fraction and oxygen content.

This work was conducted with the products resulting from the 1650°C synthesis (5-hr hold) described in Table 8. These were crushed into 1/8-in. chunks which were then reheated to 1650°C for an accumulated hold time of 8 hr. The sintered

material resulting from these experiments was comminuted to a fine powder in the 25-ml Spex mixer for 15 minutes. Compacts, 1/4-in. diameter by 1/4-in. high, were cold pressed (1/4 w/o binder added) at 30,000 psi and heated to 1650°C with an accumulated hold time of 13 hr. Finally, pellets produced in the latter resintering were heated to 1750°C and held for 1 hr.

The results of this study, shown in Table 9, indicate that an intermediate crushing step for the 1650°C products, combined with subsequent reheating, did not significantly increase the weight fraction or the oxygen content of the $M(O_xC_{1-x})$ compositions investigated.

C. Effect of Reaction Time and Temperature

To further explore the effect of reaction time and temperature on product composition, a set of experiments was performed with intended $M(O_{0.2}C_{0.8})$, $M(O_{0.5}C_{0.5})$, and $M(O_{0.6}C_{0.4})$. Compacts of the ball-milled blend of starting materials were reacted under various time-temperature conditions and the results of the experiments are shown in Table 10. The data indicated that in preparing $M(O_xC_{1-x})$ compositions by the carbon reduction of UO_2 - PuO_2 mixtures, the following heat treatment in flowing helium gave equivalent results: 5 hr at 1650°C; 3 hr at 1750°C; and 0.5 hr at 1900°C. Longer hold periods and reheating did not significantly increase the oxygen content or the weight fraction of the $M(O_xC_{1-x})$ phase. It should be further noted that the attempt to synthesize $M(O_{0.6}C_{0.4})$ at 1450°C yielded a product containing essentially MC [i.e., $x \approx 0$ in $M(O_xC_{1-x})$] and MO_2 .

D. Effect of Milling Time and Material Form

To maximize the oxygen content of the $M(O_xC_{1-x})$ phase, the synthesis of intended MO by carbon reduction in helium was also studied. Previous work on this composition produced monoxide-phase weight fractions as high as 59 w/o and oxygen contents as high as $x = 0.58$ (see Table 8). This study involved investigations

TABLE 9 — EFFECT OF RESINTERING $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ PREPARED BY CARBON REDUCTION OF UO_2 AND PuO_2 IN HELIUM

Exp. No.	Intended Composition	Synthesis Temp, °C (Accumulated Hold Time, hr)	Carbon Content in Product, w/o	Amount of $M(O_xC_{1-x})$ Phase, w/o	Calculated $M(O_xC_{1-x})$ Composition	X-Ray Diffraction Analysis	
						Phase Intensity	Lattice Parameter, Å
1	$M(O_{0.27}C_{0.73})^\dagger$	1650 (5)‡	3.40	95	$M(O_{0.25}C_{0.75})$	Major $M(O_xC_{1-x})$ Faint/weak MO_{2-x}	4.9571 ± 0.0004 Not determined
2	$M(O_{0.27}C_{0.73})$	1650 (8)§	3.39	96	$M(O_{0.26}C_{0.74})$	Major $M(O_xC_{1-x})$ Faint/weak MO_{2-x}	4.9578 ± 0.0003 Not determined
3	$M(O_{0.27}C_{0.73})$	1650 (13)¶	3.33	91	$M(O_{0.23}C_{0.77})$	Not determined on this sample	—
4	$M(O_{0.27}C_{0.73})$	1650 (13) plus 1750 (1)**	3.23	93	$M(O_{0.27}C_{0.73})$	Major $M(O_xC_{1-x})$ Weak/mod. MO_{2-x}	4.9583 ± 0.0007 Not determined
5	$M(O_{0.40}C_{0.60})$	1650 (5)‡	3.15	92	$M(O_{0.26}C_{0.72})$	Major $M(O_xC_{1-x})$ Weak MO_{2-x}	4.9569 ± 0.0009 Not determined
6	$M(O_{0.40}C_{0.60})$	1650 (8)§	3.16	89	$M(O_{0.26}C_{0.74})$	Major $M(O_xC_{1-x})$ Weak MO_{2-x}	4.9564 ± 0.0005 Not determined
7	$M(O_{0.40}C_{0.60})$	1650 (13)¶	3.19	88	$M(O_{0.24}C_{0.76})$	Not determined on this sample	—
8	$M(O_{0.40}C_{0.60})$	1650 (13) plus 1750 (1)**	3.13	89	$M(O_{0.27}C_{0.73})$	Major $M(O_xC_{1-x})$ Weak/mod. MO_{2-x}	4.9567 ± 0.0004 5.477
9	$M(O_{0.60}C_{0.40})$	1650 (5)‡	2.51	77	$M(O_{0.32}C_{0.68})$	Strong $M(O_xC_{1-x})$ Strong MO_{2-x}	4.9576 ± 0.0006 5.4762 ± 0.0019
10	$M(O_{0.60}C_{0.40})$	1650 (8)§	2.53	75	$M(O_{0.29}C_{0.71})$	Strong $M(O_xC_{1-x})$ Strong MO_{2-x}	4.9570 ± 0.0004 5.479
11	$M(O_{0.60}C_{0.40})$	1650 (13)¶	2.61	71	$M(O_{0.29}C_{0.71})$	Strong $M(O_xC_{1-x})$ Strong MO_{2-x}	4.9599 ± 0.0010 5.4778 ± 0.0005
12	$M(O_{0.60}C_{0.40})$	1650 (13) plus 1750 (1)**	2.54	78	$M(O_{0.32}C_{0.68})$	Strong $M(O_xC_{1-x})$	4.9557 ± 0.0013 5.4812 ± 0.0031

* Composition was calculated from X-ray density, point count, and carbon content.

† $M = (U_{0.9}Pu_{0.1})$.

‡ Pellets reacted in a helium flow rate of 30 ft³/hr.

§ Pellets resulting from 1650°C (5 hr) synthesis heated in a helium flow rate of 6 ft³/hr.

¶ Pellets resulting from 1650°C (8 hr) treatment were crushed, pressed into pellets, and reheated in a helium flow rate of 6 ft³/hr.

**Pellets resulting from 1650°C (13 hr) treatment heated in a helium flow rate of 6 ft³/hr.

TABLE 10 — EFFECT OF REACTION TIME AND TEMPERATURE — (U_{0.9}Pu_{0.1})(O_xC_{1-x}) PREPARED BY CARBON REDUCTION OF UO₂ AND PuO₂ IN HELIUM

Exp. No.	Intended Composition	Synthesis Temp, °C (Accumulated Hold Time, hr)	Carbon Content in Product, w/o	Amount of M(O _x C _{1-x}) Phase, w/o	Calculated M(O _x C _{1-x}) Composition *	X-Ray Diffraction Analysis	
						Phase Intensity	Lattice Parameter, Å
1	M(O _{0.6} C _{0.4})†	1450 (4)‡	2.78	58	MC	Strong M(O _x C _{1-x}) Strong MO _{2-x}	4.9622 ± 0.0008
2	M(O _{0.6} C _{0.4})	1750 (1½)‡	2.48	82	M(O _{0.37} C _{0.63})	Strong M(O _x C _{1-x}) Strong MO _{2-x}	4.9573 ± 0.0009 5.4770 ± 0.0005
3	M(O _{0.6} C _{0.4})	1750 (3)‡	2.49	84	M(O _{0.38} C _{0.62})	Strong M(O _x C _{1-x}) Strong MO _{2-x}	4.9567 ± 0.0005 5.4781 ± 0.0011
4	M(O _{0.5} C _{0.5})	1650 (5)	2.81	94	M(O _{0.37} C _{0.63})	Strong M(O _x C _{1-x}) Moderate MO _{2-x}	4.9558 ± 0.0006 5.4810 ± 0.0009
5	M(O _{0.5} C _{0.5})	1750 (1)	2.94	92	M(O _{0.33} C _{0.67})	Major M(O _x C _{1-x}) Moderate/strong MO _{2-x}	4.9572 ± 0.0005 5.4811 ± 0.0008
6	M(O _{0.5} C _{0.5})	1750 (1)‡	2.65	92	M(O _{0.40} C _{0.60})	Strong M(O _x C _{1-x}) Moderate MO _{2-x}	4.9564 ± 0.0006 5.4782 ± 0.0005
7	M(O _{0.5} C _{0.5})	1750 (3)	2.74	92	M(O _{0.37} C _{0.63})	Major M(O _x C _{1-x}) Moderate MO _{2-x}	4.9554 ± 0.0005 5.4811
8	M(O _{0.5} C _{0.5})	1900 (1/2)	2.63	94	M(O _{0.41} C _{0.59})	Major M(O _x C _{1-x}) Moderate/strong MO _{2-x}	4.9530 ± 0.0008 5.4783 ± 0.0009
9	M(O _{0.5} C _{0.5})	1550 (1) plus 1750 (1) plus 1900 (1)§	2.62	84	M(O _{0.35} C _{0.65})	Major M(O _x C _{1-x}) Weak/moderate MO _{2-x}	4.9528 ± 0.0001
10	M(O _{0.2} C _{0.8})	1650 (5)	3.68	100	M(O _{0.23} C _{0.77})	Major M(O _x C _{1-x}) Faint ind. MO _{2-x}	4.9598 ± 0.0006
11	M(O _{0.2} C _{0.8})	1750 (3)	3.62	100	M(O _{0.24} C _{0.76})	Single-phase M(O _x C _{1-x})	4.9607 ± 0.0005
12	M(O _{0.2} C _{0.8})	1900 (1/2)	3.62	100	M(O _{0.24} C _{0.76})	Single-phase M(O _x C _{1-x})	4.9596 ± 0.0005

*Composition was calculated from X-ray density, point count, and carbon content.

†M = (U_{0.9}Pu_{0.1}).

‡Wafer 0.012 to 0.025-in. thick.

§Product from Exp. 3 crushed to -200 mesh, pressed into pellets, and reheated.

of the following: (1) the effect of ball milling 72 hr instead of the usual 24 hr, (2) the effect of using UO_2 of 0.5-micron particle size rather than the usual 3-micron starting material, and (3) the effect of firing a granulated reaction mixture instead of conventional cold pressed pellets. The first two process variations were designed to produce blends more homogeneous than those reacted in previous syntheses. In the case of the third process change, it was anticipated that the CO evolved in the reaction would escape more readily from the granules than from larger, more dense, cold pressed pellets, and therefore would promote a more complete reaction.

The experimental procedure consisted of ball milling one reaction mixture of UO_2 , PuO_2 , and C for 72 hr and another mixture for only 24 hr. Carbowax-6000 (0.4 w/o of total solids) dissolved in benzene was added to the blends and approximately 1/8-in. diameter granules were formed by stirring the resulting paste. Ten grams of each batch of granules were heated in a tantalum-lined graphite crucible for 2 hr at 1750°C in flowing helium. The results in Table 11 under Experiments 1 and 2 show no substantial improvement in monoxide-phase weight fraction and oxygen content over that previously found. Furthermore, prolonged ball milling did not appear to have any beneficial effect.

To determine the effect of UO_2 particle size variation, pellets were cold pressed at 200 psi from 24-hr ball milled reaction mixtures. The data in Table 11 for the two UO_2 starting materials (Experiments 3 and 4) indicate that the products of synthesis at 1750°C were similar.

Metallographic examination of the intended MO synthesis products revealed segregation of the $\text{M}(\text{O}_x\text{C}_{1-x})$ and MO_{2-x} phases (see Fig. 6a). Therefore, an attempt was made to improve the reaction blend uniformity by substituting liquid phenol-formaldehyde resin for the powdered carbon normally used. It was anticipated that the resin would cover the MO_2 particles uniformly and that subsequent removal of gaseous products during initial heating would later provide the neces-

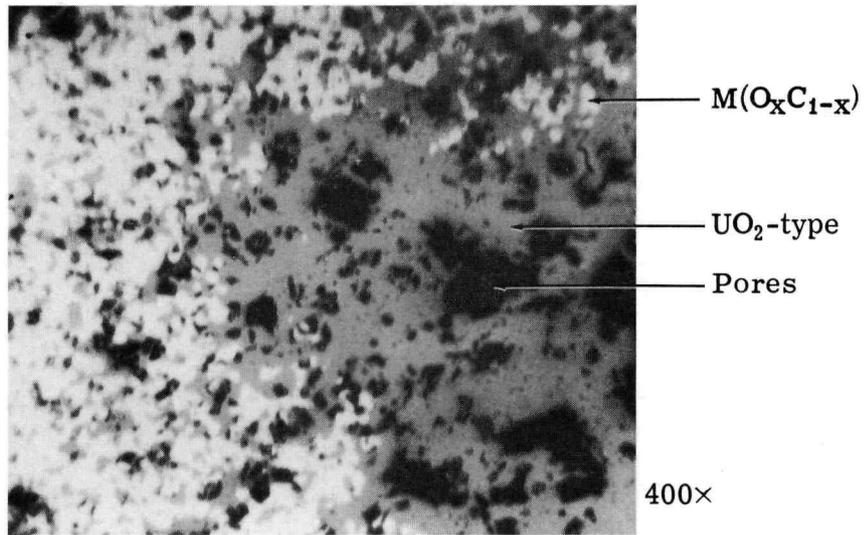
TABLE 11 — EFFECT OF MILLING TIME AND MATERIAL FORM — SYNTHESIS OF INTENDED $(U_{0.9}Pu_{0.1})O$ BY CARBON REDUCTION OF UO_2 AND PuO_2 AT $1750^\circ C$ FOR 2 HR

Exp. No.	Ball Milling Time, hr	Material Form	Amount of $M(O_xC_{1-x})$ Phase, w/o	Calculated $M(O_xC_{1-x})$ Composition*	X-Ray Diffraction Analysis (Phases Present, and Lattice Parameter, Å)	
					$M(O_xC_{1-x})$	MO_{2-x}
1	72	Granulated	58	$M(O_{0.58}C_{0.42})^\dagger$	4.9536 ± 0.0012	5.4795 ± 0.0009
2	24	Granulated	58	$M(O_{0.58}C_{0.42})$	4.9530 ± 0.0011	5.4801 ± 0.0011
3	24	Pellet	55	$M(O_{0.55}C_{0.45})$	4.9527 ± 0.0009	5.4818 ± 0.0007
4‡	24	Pellet	55	$M(O_{0.58}C_{0.42})$	4.9530 ± 0.0015	5.4807 ± 0.0018

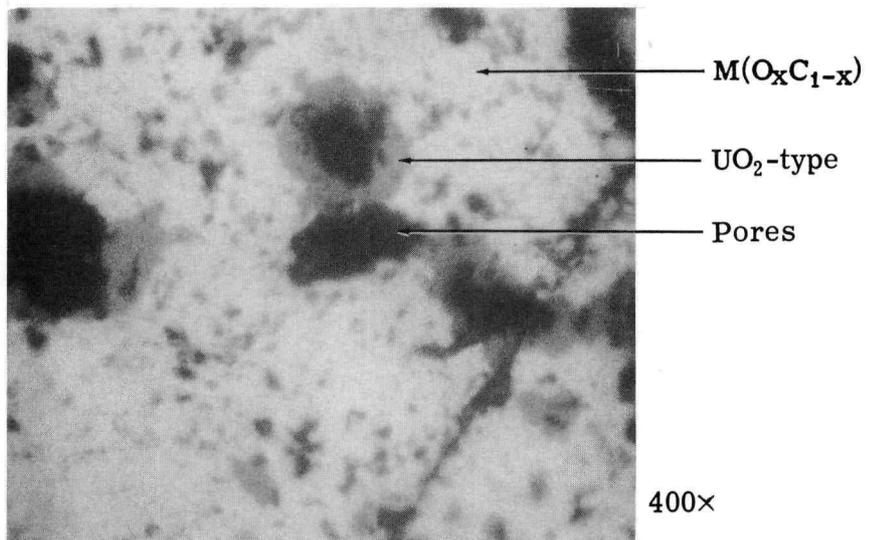
*Composition was calculated from X-ray density, point count, and carbon content.

† $M = (U_{0.9}Pu_{0.1})$.

‡Prepared with 0.5-micron UO_2 powder. The usual 3-micron UO_2 powder was used in the other experiments.



a. Product of standard carbon reduction showing nonuniform distribution of phases



b. Improved distribution after substituting phenolformaldehyde for carbon powder

Fig. 6 — Intended $(U_{0.9}Pu_{0.1})O$ Synthesized by Carbon Reduction in Helium at $1750^{\circ}C$ for 2 hr Showing Effect of Phenolformaldehyde Substitution for Carbon Powder

sary continuous network of pores for adequate CO removal. The amount of carbon residue produced by heating this resin varies from about 30 to 50%, depending upon heating conditions, i.e., rate of heating, other materials present, and atmosphere. Assuming that the carbon residue would be 35% of the original resin weight, a batch of mixed dioxides with liquid phenolformaldehyde was formulated to produce intended MO.

Compacts were pressed and cured at 150°C and heated to 1750°C for 70 minutes. The synthesis product contained 85 w/o of a calculated $M(O_{0.56}C_{0.44})$ phase. X-ray diffraction analysis indicated the usual MO_{2-x} phase ($a_0 = 5.4823 \pm 0.0020 \text{ \AA}$), and a strong $M(O_xC_{1-x})$ -type ($a_0 = 4.9523 \pm 0.0005 \text{ \AA}$).

A carbon material balance on the reaction mixture and the product obtained indicated that the original mixture contained more carbon than the stoichiometric amount required for intended MO synthesis. Nevertheless, the product homogeneity was improved (see Fig. 6b), and, although the oxygen atom fraction has not been significantly increased, this technique promises to yield higher weight fractions of the high oxygen $M(O_xC_{1-x})$ than previously obtained. Further development is required, however, to optimize the process.

F. Variation of $M(O_xC_{1-x})$ Lattice Parameter with Oxygen Content

Lattice parameter data as a function of the $M(O_xC_{1-x})$ oxygen content resulting from the carbon reduction in helium of the mixed dioxides at 1750°C are plotted in Fig. 7. The decrease in lattice parameter with increasing oxygen content is not as sharp as found in the products of uranium metal reduction at 1650°C (see Fig. 2). A possible explanation is that, with the latter method, metal dissolved in the $M(O_xC_{1-x})$ lattice contributes to the decrease in lattice parameter. The major significance of the Fig. 7 relationship, however, is that the maximum oxygen content appears to be approximately $x = 0.6$ in agreement with results from the uranium metal reduction work.

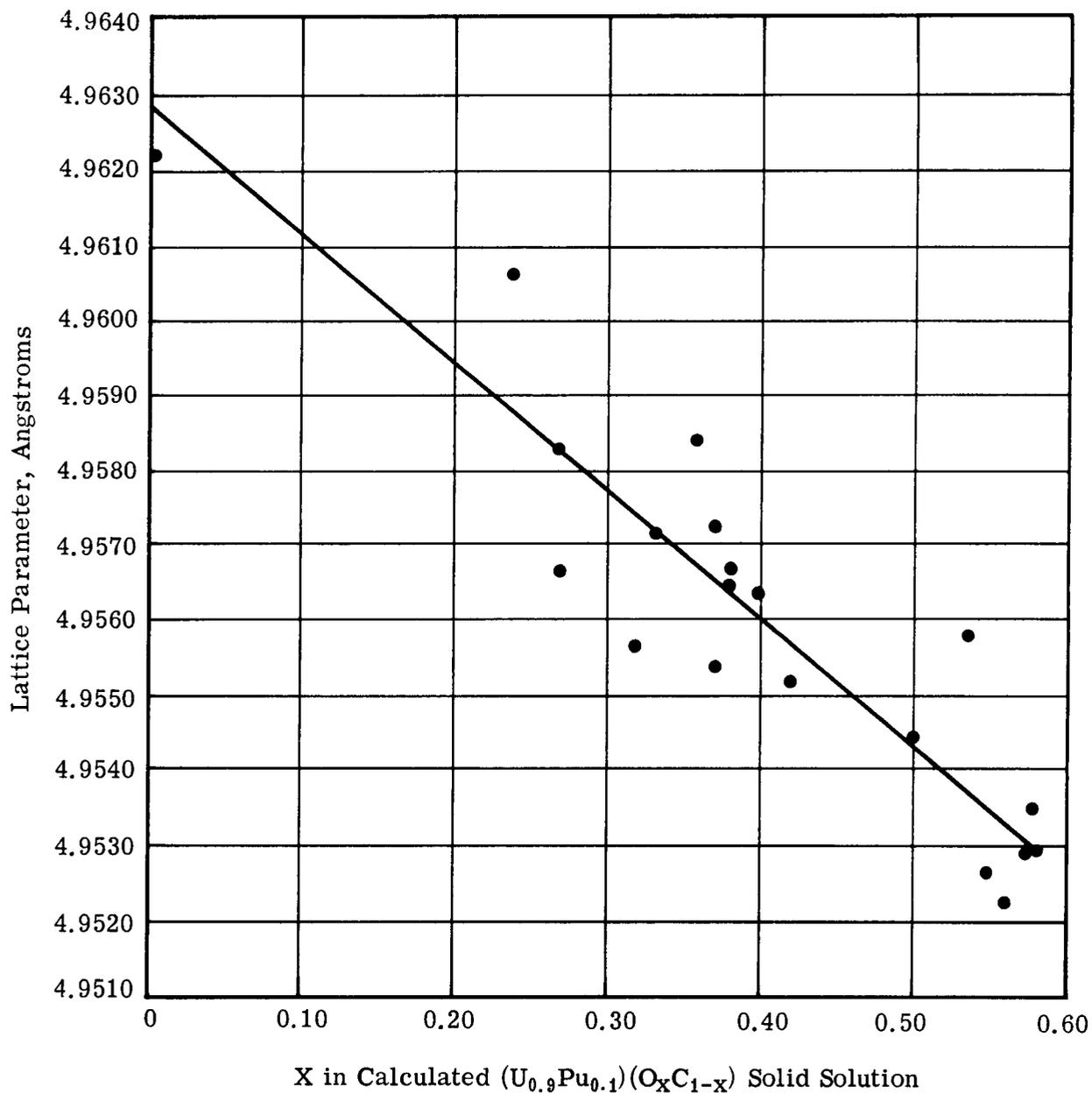


Fig. 7 — Variation of $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ Lattice Parameter with Oxygen Content. Carbon Reduction of UO_2 and PuO_2 at $1750^\circ C$.

Calculations from X-ray data indicate that the theoretical densities of $M(O_xC_{1-x})$ compositions lie in the 13.7 to 13.8 g/cm³ range.

G. Effect of CO Removal

Two experiments were performed to verify the need for removing CO from the reaction zone during the synthesis of $M(O_xC_{1-x})$ compositions by the carbon reduction method. In Experiment 1, compacts of a ball milled batch of UO_2 , PuO_2 , and carbon formulated to produce $M(O_{0.5}C_{0.5})$ were reacted at 1750°C for 3 hr in an open tantalum-lined graphite container with a helium flow of 30 ft³/hr maintained through the furnace. In Experiment 2, similar compacts were also reacted at 1750°C for 3 hr but were confined in closed-end tantalum tubes so that the atmosphere in the reaction zone was essentially static. The results, presented in Table 12, indicate that in the former run, where the CO was swept out of the system, the product contained an oxide phase and 92 w/o of a $M(O_{0.37}C_{0.63})$ phase only. However, in the product from the latter run (in static helium) the presence of an MC_2 phase was confirmed by X-ray analysis and metallography. Thus, it appears that a flow of helium prevents MC_2 formation by removing the CO reaction product.

Vacuum Experiments

Synthesis studies in vacuum (to facilitate the removal of CO) were also conducted to produce $M(O_xC_{1-x})$ compositions by carbon reduction of the mixed dioxides. The objectives were: (1) to establish a set of time-temperature conditions to yield a reaction sintered product, i.e., concurrently synthesized and densified; and (2) to compare the product compositions with those obtained from helium atmosphere syntheses. Three intended compositions were studied having x values of 0.6, 0.5, and 0.4.

The starting materials were blended in a 3-ml capacity Spex mixer for 1 hr. After blending, the mix was cold pressed without binder at 30,000 psi into com-

TABLE 12 — EFFECT OF CO PRESSURE — INTENDED $(U_{0.9}Pu_{0.1})(O_{0.5}C_{0.5})$ PREPARED BY CARBON REDUCTION OF UO_2 AND PuO_2 IN HELIUM

Exp. No.	Helium Flow Rate, ft^3/hr	Synthesis Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Amount of $M(O_xC_{1-x})$ Phase, w/o	Calculated $M(O_xC_{1-x})$ Composition*	X-Ray Diffraction Analysis	
						Phase Intensity	Lattice Parameter, Å
1	30	1750 (3)	2.74	92	$M(O_{0.37}C_{0.63})^\dagger$	Major $M(O_xC_{1-x})$ Moderate MO_{2-x}	4.9554 ± 0.0005 5.4811
2	0	1750 (3)	3.30	—	—	Major MO_{2-x} Strong $M(O_xC_{1-x})$ Weak/moderate MC_2	5.4876 ± 0.0015 4.9628 ± 0.0018

*Composition was calculated from point count, carbon content, and assumed X-ray density.

†M = $(U_{0.9}Pu_{0.1})$.

pacts 0.22-in. diameter by 0.25-in. long. The compacts were reacted in tantalum crucibles in a vacuum furnace at temperatures of 1550, 1650, and 1750°C. The hold times at temperature were varied from 0.5 to 5.0 hr, while a background pressure of less than 1-micron Hg was maintained.

The results of this survey were as follows.

1. The synthesis products after 1 hr or 5 hr at 1550°C were excessively soft and powdery, indicating that the reaction was incomplete.
2. After 0.5 hr at 1750°C, a very porous structure was produced having a thick (UPu)O₂-type skin.
3. The appearance of the materials produced after 5 hr at 1650°C indicated that a desirable degree of reaction sintering had occurred. The products were dense and the (UPu)O₂-type skin on the surface, which invariably forms in this synthesis approach, was sufficiently thin (less than 5 mils) to be ground off.
4. The 1650°C synthesis data, summarized in Table 13, show that the weight fraction and oxygen content of the monoxide phase are greater after a 5-hr hold than after a 2-hr hold. In addition, the product from the 5-hr hold is more dense than that from the 2-hr hold. This is also evident in the representative microstructure of materials produced at 1650°C shown in Figs. 8 and 9.

On the basis of these experiments, reaction sintering conditions for carbon reduction of the mixed dioxides in vacuum were established as 1650°C with a 5-hr hold. From a comparison of the data in Table 13 with those of Tables 9 and 10, it is seen that the compositions produced in vacuum were similar to those obtained in helium under these time-temperature conditions.

TABLE 13 — REACTION SINTERING OF $(U_{0.9}Pu_{0.1})(O_xC_{1-x})$ PREPARED BY CARBON REDUCTION OF UO_2 AND PuO_2 IN VACUUM

Exp. No.	Intended Composition	Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Amount of $M(O_xC_{1-x})$ Phase, w/o	Calculated $M(O_xC_{1-x})$ Composition*	Porosity, † v/o	Metallography Remarks
34	$M(O_{0.6}C_{0.4})$ ‡	1650 (2)	2.51	79	$M(O_{0.33}C_{0.67})$ ‡	11	$M(O_xC_{1-x})$, MO_2 -type
43	$M(O_{0.6}C_{0.4})$	1650 (5)	2.38	81	$M(O_{0.40}C_{0.60})$	3	$M(O_xC_{1-x})$, MO_2 -type Trace of metal
35	$M(O_{0.5}C_{0.5})$	1650 (2)	2.78	73	$M(O_{0.20}C_{0.80})$	16	$M(O_xC_{1-x})$, MO_2 -type
44	$M(O_{0.5}C_{0.5})$	1650 (5)	2.68	90	$M(O_{0.38}C_{0.62})$	2	$M(O_xC_{1-x})$, MO_2 -type Trace of metal
36	$M(O_{0.4}C_{0.6})$	1650 (2)	3.07	76	$M(O_{0.15}C_{0.85})$	21	$M(O_xC_{1-x})$, MO_2 -type
45	$M(O_{0.4}C_{0.6})$	1650 (5)	3.10	88	$M(O_{0.28}C_{0.72})$	10	$M(O_xC_{1-x})$, MO_2 -type

*Composition was calculated from point count, carbon content, and assumed X-ray density.

†By point count.

‡ $M = (U_{0.9}Pu_{0.1})$.

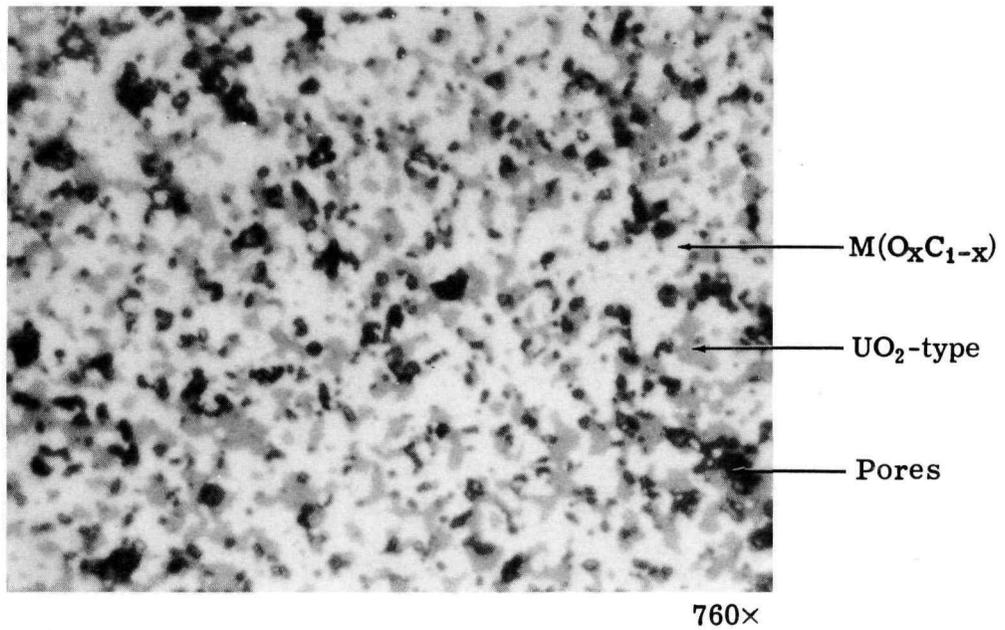


Fig. 8 — Intended $(U_{0.9}Pu_{0.1})(O_{0.6}C_{0.4})$ Synthesized by Carbon Reduction in Vacuum — 2 hr at $1650^{\circ}C$

Synthesized in vacuum by carbon reduction of UO_2 and PuO_2 at $1650^{\circ}C$, 2 hr

(Table 13, Experiment 34)

Total carbon:	2.51 w/o
$M(O_xC_{1-x})$ phase:	79 w/o
Composition:	$M(O_{0.33}C_{0.67})$

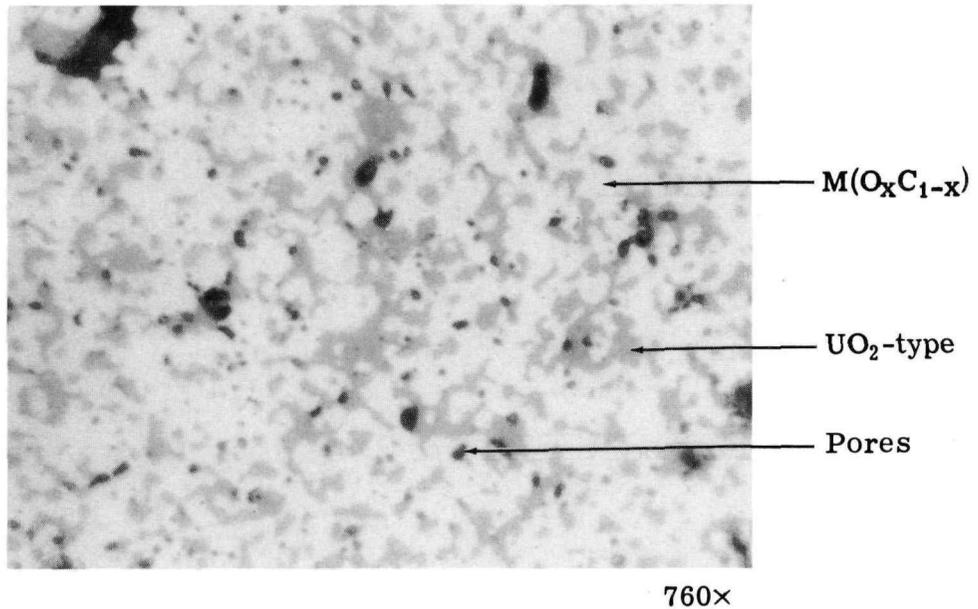


Fig. 9 — Intended (U_{0.9}Pu_{0.1})(O_{0.6}C_{0.4}) Synthesized by Carbon Reduction in Vacuum — 5 hr at 1650°C

Synthesized in vacuum by carbon reduction of
 UO₂ and PuO₂ at 1650°C, 5 hr
 (Table 13, Experiment 43)

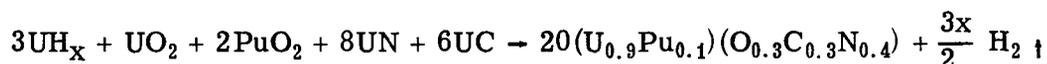
Total carbon: 2.38 w/o
 M(O_xC_{1-x}) phase: 81 w/o
 Composition: M(O_{0.40}C_{0.60})

3.3 SYNTHESIS OF (UPu)(O_xC_yN_z) COMPOSITIONS

3.3.1 Preliminary Experiments

Because boiling water corrosion tests (see Section 4.2.2) indicated that an oxygen content of $x = 0.37$ in essentially single-phase $M(O_xC_{1-x})$ was insufficient to prevent hydrolysis, a synthesis study of $M(O_xC_yN_z)$ compositions was undertaken to produce a superior water corrosion resistant material by substituting nitrogen for some of the carbon atoms in the oxygen-saturated $M(O_xC_{1-x})$ structure.

The initial syntheses utilized the uranium metal reduction in helium in which uranium hydride is the source of the metal and nitrogen and carbon are added as UN and UC, respectively, as shown in the following typical reaction:



These experiments were aimed at preparing compositions with intended oxygen contents ranging from $x = 0.2$ to 0.5 . The starting materials were blended for 30 minutes in the 25-ml Spex mixer, compacted into 1/4-in. diameter pellets at 30,000 psi, and heated at 1650°C for 5 hr in a tantalum-lined graphite crucible with a helium flow of 6 ft³/hr. The results presented in Table 14 show that several nearly single-phase compositions were produced. The most attractive material from the standpoint of minimal carbon content, Experiment 7, was reproduced in Experiment 7a in the form of 20 specimens for water corrosion tests. The relatively high product densities ranging to approximately 95% of theoretical, shown in Table 14, are indicative of the reaction sintering which occurred during synthesis.

Additional preliminary synthesis experiments were conducted in vacuum involving two synthesis routes: (1) uranium metal reduction of the mixed dioxides with UN and UC added, and (2) carbon reduction of the mixed dioxides with UN added. The intended compositions for these two sets of syntheses had the same

TABLE 14 — SYNTHESIS OF $(U_{0.9}Pu_{0.1})(O_xC_yN_z)$ BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC AND UN IN HELIUM AT 1650°C FOR 5 HR

Exp. No.	Intended Composition	Carbon Content in Product, w/o	Nitrogen Content in Product, w/o	Amount of $M(O_xC_yN_z)$ Phase, w/o	Calculated $M(O_xC_yN_z)$ Composition *	X-Ray Analysis		Pellet Density, g/cm^2
						Phase Intensity	Lattice Parameter, Å	
1	$M(O_{0.2}C_{0.5}N_{0.3})$ †	2.50	—	94	$M(O_{0.12}C_{0.56}N_{0.32})$	Major $M(O_xC_yN_z)$ Weak MO_{2-x}	4.9401 ± 0.0005	12.0
2	$M(O_{0.3}C_{0.5}N_{0.2})$	2.58	—	91	$M(O_{0.19}C_{0.59}N_{0.22})$	Major $M(O_xC_yN_z)$ Weak/mod. MO_{2-x} Faint ind. βPu_2O_3	4.9435 ± 0.0009	12.6
3	$M(O_{0.4}C_{0.5}N_{0.1})$	2.49	—	84	$M(O_{0.26}C_{0.62}N_{0.12})$	Major $M(O_xC_yN_z)$ Moderate MO_{2-x}	4.9491 ± 0.0005	12.4
4 ‡	$M(O_{0.5}C_{0.4}N_{0.1})$	2.09	0.65	80	$M(O_{0.32}C_{0.53}N_{0.15})$	Major $M(O_xC_yN_z)$ Mod./strong MO_{2-x}	4.9412 ± 0.0008	12.7
5	$M(O_{0.3}C_{0.4}N_{0.3})$	2.18	1.53	92	$M(O_{0.21}C_{0.49}N_{0.30})$	Major $M(O_xC_yN_z)$ Weak MO_{2-x}	4.9324 ± 0.0008	12.3
6	$M(O_{0.2}C_{0.3}N_{0.5})$	1.52	—	43	—	Major MO_{2-x} Mod. $M(O_xC_yN_z)$	5.4835 ± 0.0015 4.9581 ± 0.0007	11.4
7	$M(O_{0.3}C_{0.3}N_{0.4})$	1.57	—	92	$M(O_{0.21}C_{0.36}N_{0.43})$	Major $M(O_xC_yN_z)$ Weak MO_{2-x}	4.9230 ± 0.005	12.8
7a	$M(O_{0.3}C_{0.3}N_{0.4})$	1.59	2.32	91	$M(O_{0.21}C_{0.37}N_{0.42})$	Major $M(O_xC_yN_z)$ Weak/mod. MO_{2-x}	4.9248 ± 0.0013	12.3
8 §	$M(O_{0.4}C_{0.3}N_{0.3})$	1.60	—	81	$M(O_{0.21}C_{0.42}N_{0.37})$	Major $M(O_xC_yN_z)$ Moderate MO_{2-x}	4.9268 ± 0.0004	12.4

*Composition was calculated from X-ray density, point count, and carbon content. (Nitrogen assumed same as intended except in Exp. Numbers 4, 5, and 7a where analyzed.)

†M = $(U_{0.9}Pu_{0.1})$.

‡Contained 2 w/o free metal as a third phase.

§Contained 1 w/o free metal as a third phase.

oxygen content range of $x = 0.5$ to 0.8 . In no case was the attainment of a single-phase product approached. The highest $M(O_xC_yN_z)$ weight fraction in the product from the carbon reduction route was 78 w/o of an $M(O_{0.41}C_{0.50}N_{0.09})$ composition. The highest $M(O_xC_yN_z)$ content in the product from the uranium metal reduction route was 79 w/o of a $M(O_{0.20}C_{0.27}N_{0.53})$ composition.

3.3.2 Intended $(U_{0.9}Pu_{0.1})(O_xC_{0.2}N_{0.8-x})$ by Uranium Metal Reduction

To explore the effect of further minimizing the carbon content, a synthesis study was performed in which the intended carbon content was fixed at $y = 0.2$, while the intended oxygen content was varied from $x = 0.2$ to 0.6 . The reaction mixtures of UH_x , UN , UO_2 , PuO_2 , and UC were blended, compacted, and heated for 5 hr at $1650^\circ C$ in helium. The results in Table 15 indicate that metal was present in every product except where the intended O/C ratio was one. Furthermore, the metal content decreased and the monoxide weight fraction increased with decreasing intended oxygen.

Several of these syntheses were repeated in vacuum, and, as with helium, essentially single-phase materials were produced only when the intended oxygen content was $x = 0.2$.

Calculations from the lattice parameter data in Tables 14 and 15 indicate that the theoretical densities of the $M(O_xC_yN_z)$ compositions are in the 13.8 to 13.9 g/cm³ range.

The $M(O_xC_yN_z)$ weight fractions and the phases found in the products of the uranium metal reduction in helium are plotted in Fig. 10 as a function of intended composition in the pseudoternary system MO-MC-MN. In addition to showing the approximate phase regions, the diagram graphically indicates the increase in $M(O_xC_yN_z)$ weight fraction with decreasing intended oxygen content when the carbon is held constant. Anselin et al.¹³ reported a similar delineation of the phase field for the ternary $M(O_xC_yN_z)$ solid solutions in the two limiting cases where M represented uranium and plutonium, respectively.

TABLE 15 — SYNTHESIS OF $(U_{0.9}Pu_{0.1})(O_xC_{0.2}N_{0.8-x})$ BY URANIUM METAL
REDUCTION OF UO_2 AND PuO_2 WITH UN AND UC IN HELIUM

Intended Composition	Metallographic Results, Phases Present, and Amount, w/o			Calculated $M(O_xC_yN_z)$ Composition*	$M(O_xC_yN_z)$ Lattice Parameter, Å
	$M(O_xC_yN_z)$	MO_{2-x}	Metal		
$M(O_{0.6}C_{0.2}N_{0.2})^\dagger$	58	26	16	$M(O_{0.24}C_{0.42}N_{0.34})$	4.9270 ± 0.0006
$M(O_{0.5}C_{0.2}N_{0.3})$	73	16	11	$M(O_{0.26}C_{0.33}N_{0.41})$	4.9226 ± 0.0011
$M(O_{0.4}C_{0.2}N_{0.4})$	76	13	11	$M(O_{0.16}C_{0.31}N_{0.53})$	4.9173 ± 0.0003
$M(O_{0.3}C_{0.2}N_{0.5})$	88	9	3	$M(O_{0.15}C_{0.28}N_{0.57})$	4.9137 ± 0.0005
$M(O_{0.2}C_{0.2}N_{0.6})$	96	4	—	$M(O_{0.14}C_{0.24}N_{0.62})$	4.9126 ± 0.0007
$M(O_{0.2}C_{0.2}N_{0.6})^\ddagger$	96	4	—	$M(O_{0.10}C_{0.28}N_{0.62})$	—

*Composition was calculated from point count, carbon content, and X-ray density. Nitrogen content assumed to be same as intended.

$^\dagger M = (U_{0.9}Pu_{0.1})$.

‡ Pellets for water corrosion tests.

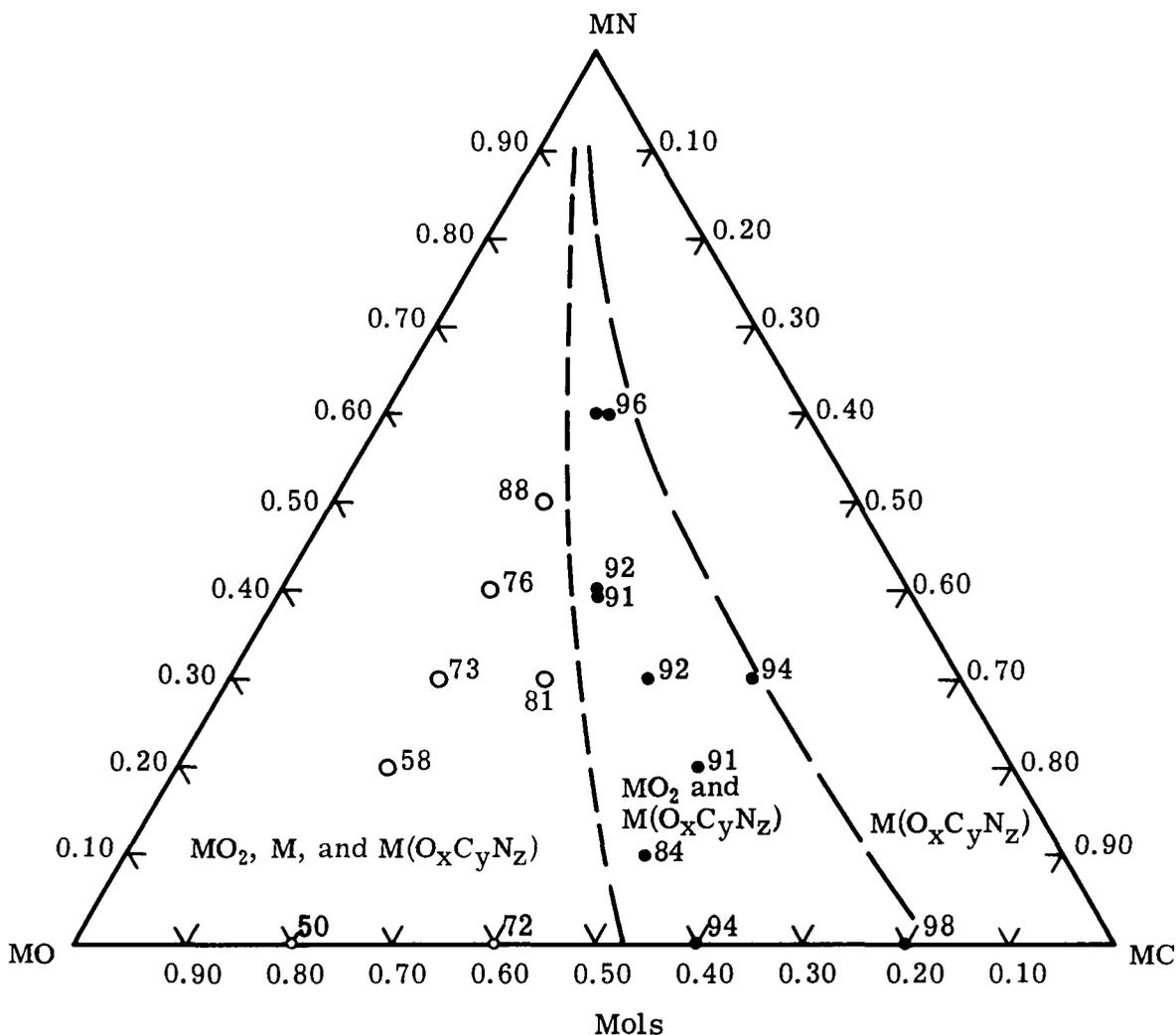


Fig. 10 — Approximate Phase Regions in the Pseudo-Ternary System MO-MC-MN Resulting from the Reaction of $\text{PuO}_2 + \text{UO}_2 + \text{UN} + \text{UC} + \text{U}$ in Helium, 1650°C (5 hr)

$\text{M} = (\text{U}_{0.9}\text{Pu}_{0.1})$

● = Two-phase product — MO_2 and $\text{M}(\text{O}_x\text{C}_y\text{N}_z)$

○ = Three-phase product — MO_2 , M, and $\text{M}(\text{O}_x\text{C}_y\text{N}_z)$

Points show intended composition; numbers show w/o of $\text{M}(\text{O}_x\text{C}_y\text{N}_z)$ phase.

3.3.3 Intended $(U_{0.9}Pu_{0.1})(O_{0.5}C_yN_{0.5-y})$ by Uranium Metal Reduction in Vacuum

Another synthesis study was undertaken to improve upon two promising $M(O_xC_yN_z)$ materials produced in the preliminary uranium metal reduction survey. These contained the highest monoxide-phase weight fractions found: 77 w/o of $M(O_{0.36}C_{0.45}N_{0.19})$ synthesized from an intended $M(O_{0.5}C_{0.4}N_{0.1})$ and 79 w/o of $M(O_{0.20}C_{0.27}N_{0.53})$ synthesized from an intended $M(O_{0.5}C_{0.2}N_{0.3})$, respectively.

Although the preliminary work was performed with the 3-micron UO_2 , the 0.5-micron UO_2 starting material was substituted in the hope that more uniform blends, and, therefore, higher $M(O_xC_yN_z)$ weight fractions would result from the finer starting material. Several reaction mixes of UH_x , UO_2 , PuO_2 , UN , and UC , formulated to produce intended $M(O_{0.5}C_{0.4}N_{0.1})$ and $M(O_{0.5}C_{0.2}N_{0.3})$, were blended, compacted, heated to $1650^\circ C$, and held for 5 hr during synthesis.

The results of the experiments are summarized in Table 16, which also includes the previous synthesis results for comparison (Experiments 50 and 51).

Although good reproducibility was achieved in the case of the intended $M(O_{0.5}C_{0.4}N_{0.1})$ syntheses, the presence of the undesirable metal phase ruled out further work on this composition.

The products from the intended $M(O_{0.5}C_{0.2}N_{0.3})$ syntheses (Experiments 63 and 65) exhibited widely varying oxygen contents ranging from $x = 0.09$ to 0.29 as compared with 0.20 for the original run (Experiment 50). These materials were relatively porous. To increase their density, the synthesis products were crushed, repressed, and sintered. The Table 16 data show that sintering, as well as reheating the sintered product (Experiment 63B), not only densified these materials but also tended to increase the oxygen content of the monoxide-type phase. Although it appeared that additional development was required to

TABLE 16 — SYNTHESIS AND SINTERING OF INTENDED $(U_{0.9}Pu_{0.1})(O_{0.5}C_yN_{0.5-y})$ BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC AND UN IN VACUUM

Exp. No.	Intended Composition	Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Nitrogen Content in Product, w/o	Metallographic Results, Phases Present, and Amount, w/o			Calculated $M(O_xC_yN_z)$ Composition*	Density, g/cm ³	Remarks
					$M(O_xC_yN_z)$	MO_{2-x}	Metal			
51†	$M(O_{0.5}C_{0.4}N_{0.1})$ ‡	1650 (5)	1.64	0.85	77	18	5	$M(O_{0.36}C_{0.45}N_{0.19})$	13.0	—
66	$M(O_{0.5}C_{0.4}N_{0.1})$	1650 (5)	1.67	0.64	79	21	Trace	$M(O_{0.41}C_{0.44}N_{0.15})$	12.3	—
50†	$M(O_{0.5}C_{0.2}N_{0.3})$	1650 (5)	1.01	2.32	79	21	—	$M(O_{0.20}C_{0.27}N_{0.53})$	—	—
63	$M(O_{0.5}C_{0.2}N_{0.3})$	1650 (5)	1.12	2.25	70	30	—	$M(O_{0.09}C_{0.33}N_{0.58})$	—	—
63A	$M(O_{0.5}C_{0.2}N_{0.3})$	1650 (1)	0.92	2.28	72	28	—	$M(O_{0.16}C_{0.27}N_{0.57})$	12.7	Sintering crushed product of Exp. No. 63
63B	$M(O_{0.5}C_{0.2}N_{0.3})$	1650 (3)	1.00	2.12	78	22	—	$M(O_{0.24}C_{0.27}N_{0.49})$	13.0	Reheating product of Exp. No. 63A
65	$M(O_{0.5}C_{0.2}N_{0.3})$	1650 (5)	1.02	1.74	74	26	—	$M(O_{0.29}C_{0.29}N_{0.42})$	10.8	—
65A	$M(O_{0.5}C_{0.2}N_{0.3})$	1650 (3)	0.99	1.75	70	30	—	$M(O_{0.26}C_{0.30}N_{0.44})$	12.2	Sintering crushed product of Exp. No. 65

*Composition was calculated from point count, carbon and nitrogen content, and assumed X-ray density.

†Previous results from Reference 4 using 3-micron UO_2 starting material.

‡M = $(U_{0.9}Pu_{0.1})$.

obtain an equilibrium product stable at 1650°C in vacuum, this work was discontinued because the attainment of a single-phase $M(O_xC_yN_z)$ composition with O/C ratio of 5/2 did not seem possible.

3.3.4 Intended $(U_{0.9}Pu_{0.1})(O_{0.3}C_yN_{0.7-y})$ by Uranium Metal Reduction in Vacuum

Helium atmosphere syntheses of intended $M(O_{0.3}C_{0.3}N_{0.4})$ and $M(O_{0.3}C_{0.4}N_{0.3})$ by uranium-metal reduction had yielded nearly single-phase $M(O_xC_yN_z)$ in the preliminary studies (see Table 14). The objective of these additional experiments was to determine the effect on composition of synthesizing in vacuum. Synthesis temperature variations from 1550 to 1750°C were investigated. Also, the effect on composition and density of sintering the crushed and repressed synthesis products at 1650°C was examined. The results for intended $M(O_{0.3}C_{0.3}N_{0.4})$ and $M(O_{0.3}C_{0.4}N_{0.3})$ are presented in Tables 17 and 18, respectively.

With both compositions, synthesis at 1750°C was accompanied by a relatively large weight loss which was attributed to volatilization of uranium metal. At 1550°C, on the other hand, weight losses were small and the weight fractions as well as the oxygen contents of the monoxide phases were at least as high as obtained from higher temperature syntheses. However, the synthesis product densities were relatively low. Invariably a density improvement was achieved by sintering the crushed synthesis products. An example is illustrated in Fig. 11. Such dense structures were preferred for water corrosion tests.

3.3.5 Intended $(U_{0.9}Pu_{0.1})(O_xC_yN_z)$ by Carbon Reduction in Vacuum

The preliminary synthesis survey by carbon reduction in vacuum involved intended oxygen contents of $x = 0.5$ to 0.8 and produced $M(O_xC_yN_z)$ weight fractions as high as 78 w/o. Higher weight fractions were sought by synthesis of the following intended compositions using this method: $M(O_{0.4}C_{0.3}N_{0.3})$, $M(O_{0.3}C_{0.4}N_{0.3})$,

TABLE 17 — SYNTHESIS AND SINTERING OF INTENDED $(U_{0.9}Pu_{0.1})(O_{0.3}C_{0.3}N_{0.4})$ BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC AND UN IN VACUUM

Exp. No.	Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Nitrogen Content in Product, w/o	Metallographic Results, Phases Present, and Amount, w/o			Calculated $M(O_xC_yN_z)$ Composition*	Density, g/cm ³	Remarks
				$M(O_xC_yN_z)$	MO_{2-x}	Metal			
73	1750 (5)	1.38	2.77	94	6	—	$M(O_{0.17}C_{0.30}N_{0.53})^\dagger$	12.0	8% weight loss
71	1650 (5)	1.46	2.63	90	9	1	$M(O_{0.13}C_{0.34}N_{0.53})$	10.4	2% weight loss
69	1650 (5)	1.34	2.06	88	12	—	$M(O_{0.27}C_{0.31}N_{0.42})$	13.2	—
75	1620 (5)	1.46	2.51	81	17	2	$M(O_{0.06}C_{0.38}N_{0.56})$	11.5	1.5% weight loss
77	1550 (5)	1.50	2.34	96	4	—	$M(O_{0.24}C_{0.32}N_{0.44})$	11.5	1.1% weight loss
77A	1650 (3)	1.43	1.70	93	7	—	$M(O_{0.36}C_{0.32}N_{0.32})$	11.3	Sintering of Exp. 77 product

*Composition was calculated from point count, carbon and nitrogen content, and assumed X-ray density.

$^\dagger M = (U_{0.9}Pu_{0.1})$.

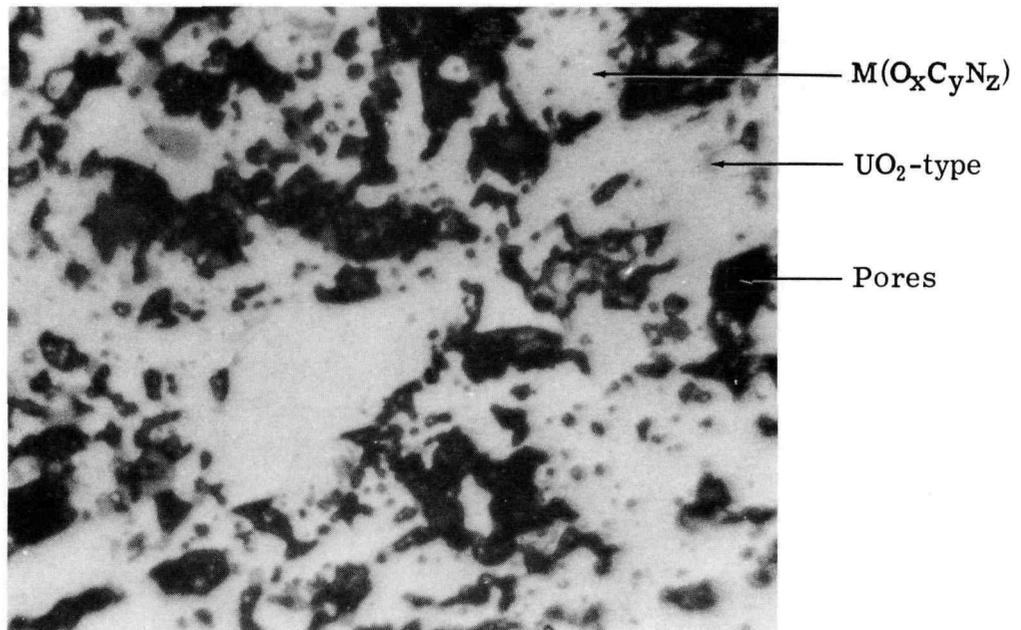
TABLE 18 — SYNTHESIS AND SINTERING OF INTENDED $(U_{0.9}Pu_{0.1})(O_{0.3}C_{0.4}N_{0.3})$ BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC AND UN IN VACUUM

Exp. No.	Temp, °C (Hold Time, hr)	Carbon Content in Product, w/o	Nitrogen Content in Product, w/o	Metallographic Results, Phases Present, and Amount, w/o			Calculated $M(O_xC_yN_z)$ Composition*	Density, g/cm ³	Remarks
				$M(O_xC_yN_z)$	MO_{2-x}	Metal			
74	1750 (5)	1.22	2.28	96	1	3	$M(O_{0.31}C_{0.27}N_{0.42})^\dagger$	12.5	33% weight loss
72	1650 (5)	1.98	1.73	93	7	—	$M(O_{0.22}C_{0.45}N_{0.33})$	10.9	3% weight loss
72A	1650 (3)	1.78	1.84	92	8	—	$M(O_{0.23}C_{0.41}N_{0.36})$	13.0	Sintering of Exp. No. 72 product
70	1650 (5)	2.00	1.73	91	9	—	$M(O_{0.21}C_{0.45}N_{0.34})$	13.2	—
76	1620 (5)	1.93	1.74	79	21	—	$M(O_{0.08}C_{0.52}N_{0.40})$	11.4	2% weight loss
76A	1650 (3)	1.94	1.78	95	5	—	$M(O_{0.24}C_{0.43}N_{0.33})$	12.5	Sintering of Exp. No. 76 product
78	1550 (5)	1.94	1.75	93	7	—	$M(O_{0.23}C_{0.43}N_{0.34})$	11.3	1.4% weight loss
78A	1650 (3)	1.82	1.65	94	5	1	$M(O_{0.28}C_{0.41}N_{0.31})$	11.7	Sintering of Exp. No. 78 product
79	1550 (5)	1.93	1.70	96	4	—	$M(O_{0.27}C_{0.42}N_{0.31})$	—	—
79A	1650 (3)	1.85	1.69	93	7	—	$M(O_{0.20}C_{0.42}N_{0.38})$	11.4‡	Sintering of Exp No. 79 product

*Composition calculated from point count, carbon and nitrogen content, and assumed X-ray density.

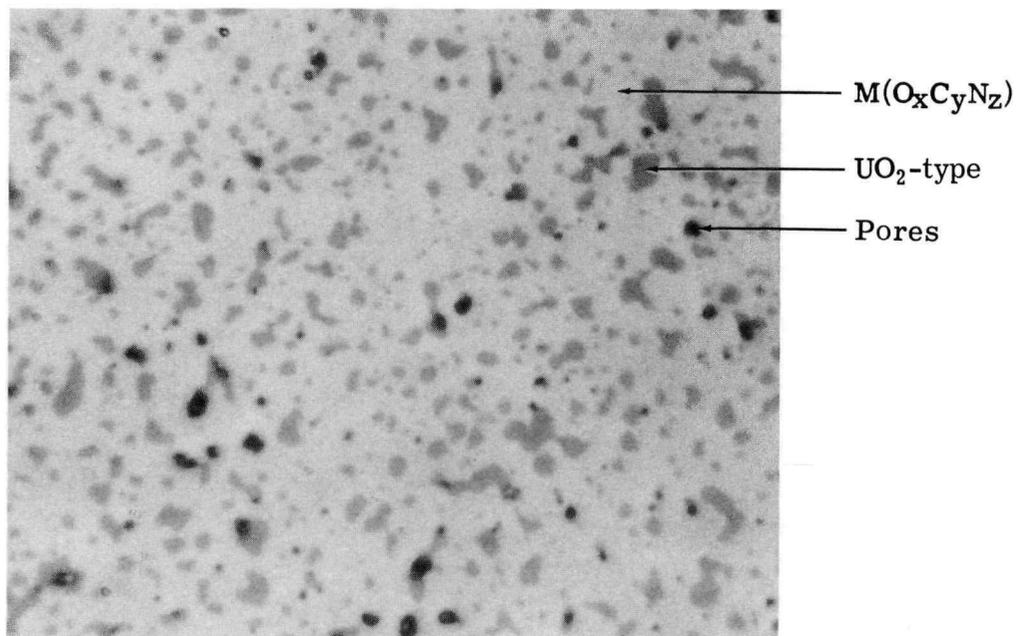
†M = $(U_{0.9}Pu_{0.1})$.

‡Density determined on surface ground pellet; all other densities reported on as-fired pellets.



520×

Synthesis Product



520×

Sintered Product

Fig. 11 — Density Improvement on Sintering Intended $(U_{0.9}Pu_{0.1})(O_{0.3}C_{0.4}N_{0.3})$ Synthesis Product (Table 18, Exp. Nos. 72 and 72A)

and $M(O_{0.3}C_{0.3}N_{0.4})$. The starting materials (C, PuO_2 , UO_2 , and UN) were blended, compacted, heated to $1650^\circ C$, and held for 5 hr.

The results of product characterization are shown in Table 19. The data show that $M(O_xC_yN_z)$ phase weight fractions ranging from 88 to 97 w/o were obtained. Although the product of the intended $M(O_{0.3}C_{0.4}N_{0.3})$ synthesis yielded the highest weight fraction, its density was the lowest of the three materials. In general, lower synthesis product densities than those obtained from uranium-metal reduction were expected because of porosity derived from CO evolution during the carbon reduction process.

3.4 SYNTHESIS OF INTENDED $(U_{0.9}Pu_{0.1})(O_xN_{1-x})$ COMPOSITIONS

Prior to the study of $M(O_xC_yN_z)$ compositions, the feasibility of synthesizing a monoxide-type material stabilized with nitrogen alone was investigated. It was expected that a $M(O_xN_{1-x})$ composition, if it could be produced, would exhibit a better thermal conductivity than that of $(UPu)O_2$ and would have good water corrosion resistance. The synthesis reaction studied was



with U in the form of uranium hydride. Intended oxygen contents ranging from $x = 0.5$ to 0.9 were covered. In addition, an intended composition with $x = 0.2$ was included as representative of the lower and less desirable oxygen range.

Compacts of the reactants were blended and pressed in the usual manner, and heated in vacuum under three sets of temperature-time conditions: $1650^\circ C$ for 2 hr; $1650^\circ C$ for 5 hr; and $1750^\circ C$ for 3 hr.

None of these conditions produced monoxide materials in which a $M(O_xN_{1-x})$ phase definitely could be identified. The major phases present were the nitride and an oxygen deficient dioxide as confirmed by X-ray diffraction analysis.

TABLE 19 — SYNTHESIS OF $(U_{0.9}Pu_{0.1})(O_xC_yN_z)$ BY CARBON REDUCTION OF UO_2 AND PuO_2 WITH UN IN VACUUM AT $1650^\circ C$ FOR 5 HR

Exp. No.	Intended Composition	Carbon Content in Product, w/o	Nitrogen Content in Product, w/o	Metallographic Results, Phases Present, and Amount, w/o			Calculated $M(O_xC_yN_z)$ Composition*	Density, g/cm^3
				$M(O_xC_yN_z)$	MO_{2-x}	Metal		
80	$M(O_{0.4}C_{0.3}N_{0.3})^\dagger$	1.88	1.49	88	12	—	$M(O_{0.25}C_{0.45}N_{0.30})$	10.6
81	$M(O_{0.3}C_{0.3}N_{0.4})$	1.81	1.88	92	8	—	$M(O_{0.22}C_{0.41}N_{0.37})$	11.2
82	$M(O_{0.3}C_{0.4}N_{0.3})$	2.17	1.47	97	3	—	$M(O_{0.26}C_{0.48}N_{0.26})$	9.7

*Composition was calculated from point count, carbon and nitrogen content, and assumed X-ray density.

$\dagger M = (U_{0.9}Pu_{0.1})$.

It appears, therefore, that the solubility of oxygen in MN is very small so that the synthesis of $M(O_xN_{1-x})$ containing a substantial oxygen content is not feasible. This result is analogous to that reported by Henry⁷ in his study of the UO-UN system.

3.5 SYNTHESIS OF INTENDED PuO and $Pu(O_xC_{1-x})$ COMPOSITIONS

A synthesis study was also conducted to produce a pure or carbon-stabilized plutonium monoxide, i.e., PuO or $Pu(O_xC_{1-x})$, which could be used as a reference material. The carbon reduction route was employed so that the starting materials were PuO_2 or βPu_2O_3 and carbon. These were blended to yield intended compositions having oxygen contents ranging from 0.42 to 1.0. Compacts of the reactants were heated in either helium or vacuum.

The results of synthesizing at temperatures ranging from 1350 to 1750°C are summarized in Table 20. The data show that a pure monoxide could not be synthesized and that the highest estimated oxygen content in the $Pu(O_xC_{1-x})$ compositions produced was $x = 0.6$.

No difference was noted between the product obtained from PuO_2 and that obtained from βPu_2O_3 . However, reaction in vacuum was more rapid with βPu_2O_3 than with PuO_2 . Also, a high $Pu(O_xC_{1-x})$ vaporization rate was observed in the 1650°C synthesis in vacuum.

3.6 SYNTHESIS OF (METAL-Pu)O COMPOSITIONS

In another effort to produce a high melting point plutonium monoxide-type compound, the possibility of preparing solid solutions of PuO with inert diluents, such as CaO , MgO , and SrO , was investigated. The latter satisfied the requirement that the diluents should be stable metal monoxides having low thermal neutron absorption cross section and high melting points. To synthesize such solid solutions the reduction of PuO_2 with CaH_2 , MgH_2 and SrH_2 , corresponding

TABLE 20 — SYNTHESIS OF INTENDED PuO and Pu(O_xC_{1-x}) BY CARBON REDUCTION OF PuO₂ OR β Pu₂O₃

Intended Product	In Helium Atmosphere		In Vacuum	
	Temp, °C	Actual Product	Temp, °C	Actual Product
PuO	1350	β Pu ₂ O ₃ , α Pu ₂ O ₃ , PuO ₂ , C	1450	β Pu ₂ O ₃ , 30 v/o Pu(O _{0.4} C _{0.6})
PuO	1550 to 1750	β Pu ₂ O ₃ , Pu(O _x C _{1-x})*	1450 to 1650	β Pu ₂ O ₃ , Pu(O _x C _{1-x})†
Pu(O _{0.9} C _{0.1})	1550 to 1750	β Pu ₂ O ₃ , Pu(O _x C _{1-x})*	1450 to 1650	—
Pu(O _{0.8} C _{0.2})	1550 to 1750	β Pu ₂ O ₃ , Pu(O _x C _{1-x}), † Pu ₂ C ₃	1450 to 1650	β Pu ₂ O ₃ , 30 v/o Pu(O _{0.4} C _{0.6})
Pu(O _{0.6} C _{0.4})	1550 to 1750	β Pu ₂ O ₃ , Pu(O _x C _{1-x}), † Pu ₂ C ₃	1450 to 1650	—
Pu(O _{0.42} C _{0.48})	1550 to 1750	β Pu ₂ O ₃ , Pu ₂ C ₃	1450 to 1650	β Pu ₂ O ₃ , 50 v/o Pu(O _{0.4} C _{0.6}), Pu ₂ C ₃

*x estimated at 0.4 to 0.6.

†x not estimated.

to the respective monoxides, was attempted. Diluent metal-to-plutonium ratios of 8:2, 6:4, and 5:5 were investigated and the reductions were conducted at temperatures up to 1750°C in helium.

Evaluation of the products involved metallography, X-ray diffraction, and chemical analysis, and, except for one material, no monoxide-type phase was detected. A small amount of such a phase was observed in the case of intended $(Ca_{0.5}Pu_{0.5})O$ which was probably stabilized by the presence of 2000 ppm carbon also found in the product. On the basis of these results, it was concluded that the mutual solubility of PuO and these alkaline earth monoxides was very small.

4. FUEL EVALUATION

4.1 INTRODUCTION

Promising monoxide-type materials consisting of essentially single-phase compositions of $M(O_xC_{1-x})$ and $M(O_xC_yN_z)$ were evaluated for water corrosion resistance to establish their applicability for water-cooled reactors. Specimens were corrosion tested first in room temperature water, then in boiling water. Those which survived these tests were subjected to an autoclave test at 550°F.

In addition, comparative thermal conductivities were estimated from room temperature thermal diffusivity measurements.

4.2 WATER CORROSION

4.2.1 Room Temperature Tests

The room temperature water corrosion tests were carried out in a nitrogen atmosphere glove box by suspending specimens from a balance into distilled water. Weight losses were measured periodically. Of two nearly single-phase $M(O_xC_{1-x})$ compositions tested, the one with the lower oxygen content, $M(O_{0.19}C_{0.81})$, disintegrated after 30 hr. The one with the higher oxygen content, $M(O_{0.37}C_{0.63})$, showed no sign of corrosion after 210 hr. Specimens containing 92 w/o of $M(O_{0.21}C_{0.49}N_{0.30})$ and 80 w/o of $M(O_{0.32}C_{0.53}N_{0.15})$ were unaffected by 100-hr exposure to room temperature water.

4.2.2 Boiling Water Tests

Boiling water tests were conducted on $M(O_xC_{1-x})$ compositions similar to those which survived exposure at room temperature and on 14 $M(O_xC_yN_z)$ compositions. The test consisted of immersing each specimen in a separate flask of boiling water in a nitrogen atmosphere glove box. The compositions tested and the results are presented in Table 21.

Although all specimens containing $M(O_xC_{1-x})$ compositions disintegrated within 1 hr, several $M(O_xC_yN_z)$ compositions survived exposure to boiling water for as long as 286 hr. A comparison of the $M(O_xC_yN_z)$ compositions in Table 21 indicates that, generally, those with carbon contents of $y > 0.4$ disintegrated in boiling water while those with $y < 0.4$ survived the boiling water test. A specimen of one of the latter materials is shown in Fig. 12 before and after the test.

It is noteworthy that effervescence of the disintegrated material was observed during cooling of the flasks, indicating that a gas generating hydrolysis reaction was occurring.

4.2.3 Autoclave Tests

Additional specimens of four of the $M(O_xC_yN_z)$ compositions not affected by boiling water, as noted in Table 21, were subjected to autoclaving in distilled deoxygenated water at 550°F using the apparatus shown in Fig. 13.

The apparatus consisted of an autoclave furnace and piping system which were located within a nitrogen atmosphere glove box, and a control panel located outside the box. Two autoclaves (Kuentzel bombs), each of approximately 100-ml capacity, were heated simultaneously within the furnace.

Analysis of the water by the modified spectrophotometric Winkler method* indi-

*Procedure published in ORNL Master Analytical Manual.

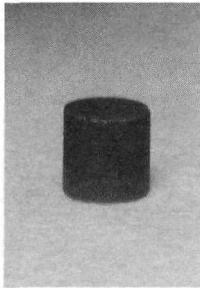
TABLE 21 — BOILING WATER CORROSION TESTS

<u>Specimen Designation</u>	<u>Composition*</u>	<u>Monoxide Phase, w/o†</u>	<u>Density, % TD</u>	<u>Test Duration, hr</u>	<u>Weight Change, %</u>	<u>Diameter Change, %</u>	<u>Height Change, %</u>	<u>Remarks</u>
<u>Materials Passing Test</u>								
Run 77A‡	M(O _{0.36} C _{0.32} N _{0.32})	93	91	286	0.03	+0.84	+1.02	All specimens darkened, a small amount of spalling observed ↓
Run 76A	M(O _{0.24} C _{0.43} N _{0.33})	95	93	24.0	-0.06	-0.10	0	
Lot 80‡ (Pellet No. 5)	M(O _{0.21} C _{0.37} N _{0.42})	91	92	73.5	-1.81	+0.37	+0.21	
Lot 80 (Pellet No. 9)	M(O _{0.21} C _{0.37} N _{0.42})	91	92	73.5	+0.09	0	+0.16	
Lot 80 (Pellet No. 2)	M(O _{0.21} C _{0.37} N _{0.42})	91	92	137	-0.26	+0.21	+0.05	
Lot 80 (Pellet No. 4)	M(O _{0.21} C _{0.37} N _{0.42})	91	89	137	-0.28	-0.05	-0.05	
Lot S-85‡	M(O _{0.10} C _{0.28} N _{0.62})	96	90	135	+0.18	-0.05	+0.05	
Run 83‡	M(O _{0.04} C _{0.21} N _{0.75})	97	80	42.75	-1.0	-0.10	+0.04	
<u>Materials Failing Test</u>								
Lot 74 (2 pellets)	M(O _{0.37} C _{0.63})	96	93	< 1	—	—	—	Specimens disintegrated ↓
Lot 79 (2 pellets)	M(O _{0.32} C _{0.68})	91	96	< 1	—	—	—	
Run 82	M(O _{0.26} C _{0.48} N _{0.26})	97	74	2.0	—	—	—	Approximately 1/3 disintegrated Specimen disintegrated Specimen cracked during test
Run 80	M(O _{0.25} C _{0.45} N _{0.30})	88	80	18.5	—	—	—	
Run 66	M(O _{0.41} C _{0.44} N _{0.15}) §	79	96	1.5	—	—	—	
Run 79A	M(O _{0.20} C _{0.42} N _{0.38})	93	84	42.75	-27.3	—	—	
Run 81	M(O _{0.22} C _{0.41} N _{0.37})	92	84	2.0	—	—	—	
Run 84	M(O _{0.05} C _{0.22} N _{0.73}) §	86	81	22.25	- 0.45	+3.9	+3.8	

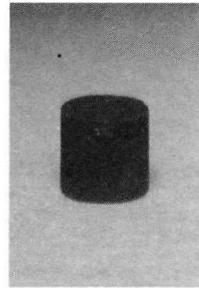
*M = (U_{0.9}Pu_{0.1}).†The balance of the material consisted of an MO₂ phase and metal where indicated.

‡Materials subsequently autoclave tested at 550°F.

§Trace of metal present.

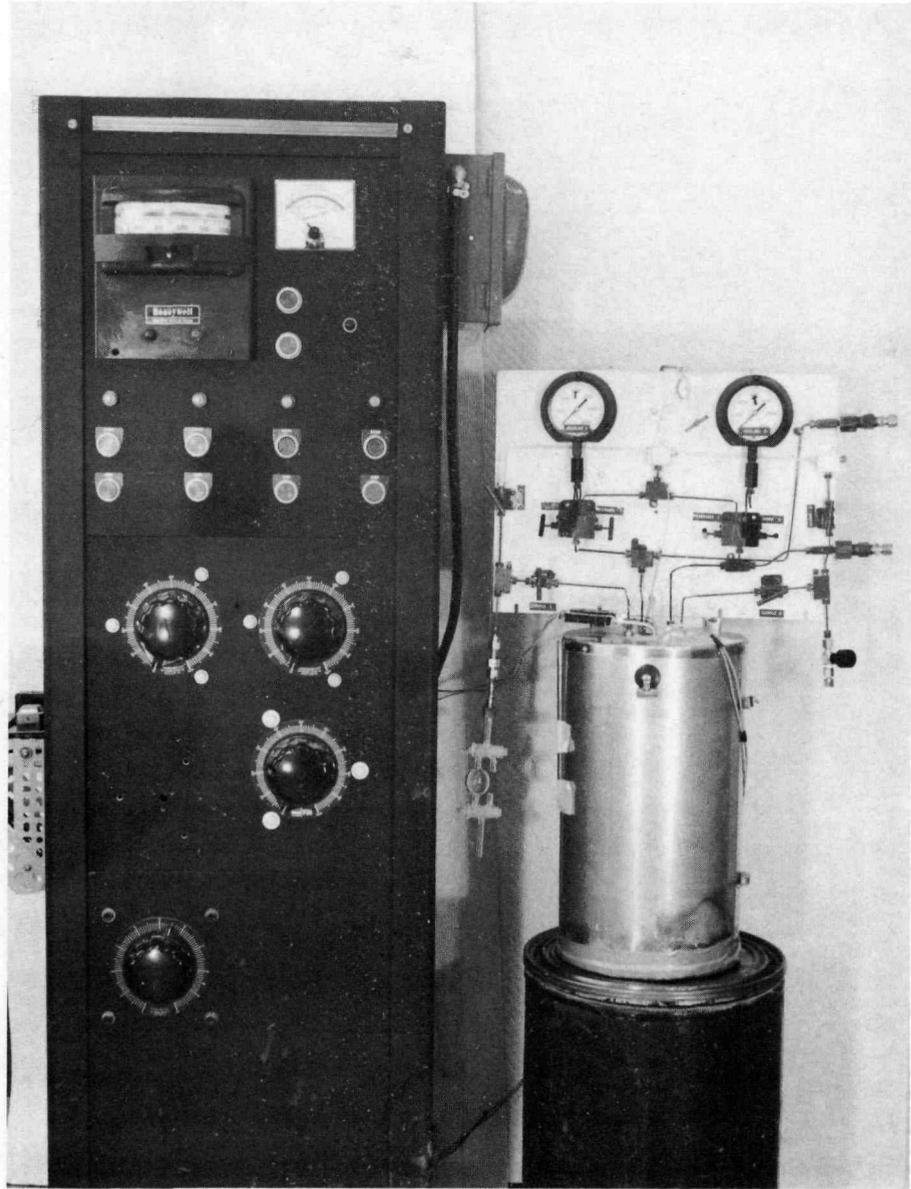


a. Before exposure



b. After exposure

Fig. 12 — Appearance of Specimen Containing 91 w/o $(U_{0.9}Pu_{0.1})(O_{0.21}C_{0.37}N_{0.42})$ before and after 137-hr Test in Boiling Water



Neg. No. 4783

Fig. 13 — View of Autoclave Furnace, Piping, and Control Panel
(Before Installation in Glove Box)

cated that an oxygen level of 0.2 ppm or less was achieved by a steam bleed-off technique with the autoclave temperature maintained above 212°F.

All $M(O_xC_yN_z)$ compositions tested disintegrated within 1 hr, while a $(UPu)O_2$ specimen containing 10 w/o Pu survived exposure to similar autoclave conditions. X-ray diffraction analysis indicated that the finely divided hydrolysis product from these tests was a dioxide-type material.

4.3 THERMAL CONDUCTIVITY

A thermal diffusivity measuring apparatus was employed to obtain comparative room temperature thermal conductivities for monoxide-type materials, dioxides, and carbide. The apparatus utilized an axial heat flow, transient technique in which cylindrical specimens of the materials were placed between an elevated temperature heat sink (up to 50°C) and a thermocouple. The rate of temperature rise of the specimen surface, opposite the surface being heated, was a measure of the thermal diffusivity.

Thermal conductivities were determined from surface temperature vs time curves using theoretical heat conduction relations plotted by McAdams¹⁴ for a semiinfinite solid. In the case of UC and UO_2 , thermal conductivities were calculated using reported heat capacity values¹⁵ of 0.048 cal/g-°C and 0.060 cal/g-°C, respectively. An assumed value of 0.048 cal/g-°C was employed in the case of the monoxide-type materials because of the similarity of their molecular structures with that of carbide.

The calculated values presented in Table 22 show that the monoxide-type compositions have higher room temperature conductivities than those of $(UPu)O_2$ and UO_2 . Although the absolute values for UC and UO_2 are lower than expected, the relative values are reasonably good. The Table 22 data, therefore, are believed to be useful for a qualitative comparison.

TABLE 22 — THERMAL CONDUCTIVITY VALUES FROM THERMAL DIFFUSIVITY MEASUREMENTS AT 32°C

<u>Material</u>	<u>Thermal Conductivity*</u>		<u>Porosity, %</u>
	<u>Btu/hr-ft-°F</u>	<u>w/cm-°C</u>	
UC + 0.1 w/o Ni	7.3	0.127	5
93 w/o M(O _{0.22} C _{0.35} N _{0.43}) + 7 w/o MO _{2-x} †	5.2	0.090	8
90 w/o M(O _{0.34} C _{0.66}) + 10 w/o MO _{2-x}	4.8	0.083	8
90 w/o M(O _{0.22} C _{0.43} N _{0.35}) + 10 w/o MO _{2-x}	4.4	0.076	24
MO ₂	3.7	0.064	2
UO ₂	2.1	0.036	2

*Uncorrected for porosity.

†M = (U_{0.9}Pu_{0.1}).

5. CONCLUSIONS

The major conclusions derived from these studies are as follows:

1. A pure monoxide, MO, cannot be made in bulk form. Essentially single-phase carbon-stabilized compositions, $M(O_xC_{1-x})$, can be reproducibly synthesized by uranium metal or carbon reduction of the mixed dioxides in helium. The maximum oxygen content is approximately $x = 0.4$. Similar products are obtained from carbon reduction in vacuum; however, uranium metal reduction in vacuum usually results in the presence of undesirable metal phase in the product.
2. Higher oxygen contents (approaching $x = 0.6$) can be produced by the carbon reduction route; but, the product also contains a substantial amount of a dioxide-type phase.
3. The uranium metal reduction in helium is not a satisfactory method of producing $M(O_xC_{1-x})$ compositions with oxygen contents greater than $x = 0.4$ because a metal phase is invariably obtained.
4. Monoxide compositions stabilized with both carbon and nitrogen, i.e., $M(O_xC_yN_z)$, can be synthesized by carbon and uranium metal reduction. Weight fractions of 90 w/o or greater are obtained when the intended oxygen content is no greater than $x = 0.3$ and the intended oxygen-to-carbon atom ratio is no more than 1.

5. The synthesis of a nitrogen-stabilized monoxide, i.e., $(UPu)(O_xN_{1-x})$, is not possible because of the apparent low oxygen solubility in the nitride.
6. As in the case of $(UPu)O$, pure PuO cannot be made in bulk form. Carbon stabilized compositions, $Pu(O_xC_{1-x})$, can be synthesized with an estimated maximum oxygen content of $x = 0.6$. Also, it appears that solid solutions of PuO with CaO , MgO , and SrO do not exist.
7. Based on unfavorable test results in $550^\circ F$ water, the corrosion resistance of the essentially single-phase monoxide-type materials produced in this program is deemed unsatisfactory for water-cooled reactors.
8. Comparative thermal diffusivity measurements indicate that monoxide-type compositions have higher room temperature thermal conductivities than those of the dioxides.

6. APPENDIX

6.1 PROPERTIES OF STARTING MATERIALS

6.1.1 Spectrographic Analysis and Properties of Dioxides and Carbon

Element, ppm	<u>UO₂</u>		<u>PuO₂</u>	<u>Carbon*</u>
	<u>Lot 60</u>	<u>Lot 78</u>		
Aluminum	—	6	10	4
Boron	0.4	<0.20	1	3
Cadmium	<0.02	<0.10	5	—
Calcium	—	<20	—	—
Chromium	13	16	30	0.1
Copper	<12	4	10	0.2
Iron	51	55	~300	20
Lead	—	<1	10	0.05
Magnesium	—	14	20	5
Manganese	<6	<5	50	0.1
Molybdenum	<1	—	1	5
Nickel	102	10	50	0.1
Tin	—	<1	1	0.1
Silicon	76	48	10	95
Vanadium	<20	—	1	—
Particle Size, μ	3	0.5	1	<1
O/M Ratio	2.08	2.11	2.02	—

*Typical analysis.

6.1.2 Chemical Analysis of Other Starting Materials

<u>Element</u>	<u>UH_x</u>	<u>UC</u>	<u>UN</u>
Oxygen	0.17 w/o	0.77 w/o	—
Carbon	0.04 w/o	4.81 w/o	0.03 w/o
Nitrogen	469 ppm	328 ppm	5.42 w/o

6.2 CHARACTERIZATION PROCEDURES

6.2.1 Metallography

A pellet specimen from each synthesis experiment was examined metallographically. After mounting in a thermosetting resin (Laminac) a rough polishing through 180, 240, and 600 SiC grits was performed on a grinding wheel followed by final polishing on a Syntron vibratory lapping-polishing machine with 0.3 μ alumina. Alternatively, the latter was done on a polishing wheel using 0.3 μ alumina followed by 3 μ diamond. Anhydrous methyl alcohol was used to rinse the mounts.

Specimens were examined in the unetched condition with a Unitron Metallograph employing a xenon light source. Under these conditions the $M(O_xC_{1-x})$ and $M(O_xC_yN_z)$ phases appeared white, the MO_{2-x} -type phase appeared gray, and any metal phase had a bright lustrous appearance. The presence of metal phase was checked with a bromine-methyl alcohol etch.

6.2.2 Point Counting

Point counting to determine the volume fraction of each phase present was performed on the unetched microstructure of the metallographic specimens. The measurements utilized a two-dimensional systematic point count technique¹⁶ which employed a sheet of transparent linear graph paper superimposed on either a photomicrograph or the image projected on the ground glass of the metallograph. Magnifications of 400 \times , 520 \times , or 720 \times were used. The number of counts taken ranged from 500 to 1000 per sample.

6.2.3 Chemical Analysis

Carbon was determined gravimetrically by combustion in oxygen using either a LECO carbon analyzer (Model 521) or a modified Fisher Induction Carbon Apparatus. Accuracy of the analysis, which was dependent upon sampling error, was estimated to lie between ± 0.01 and ± 0.1 w/o.

Nitrogen analysis was performed by a modified Kjeldahl technique. The accuracy of this analysis was estimated to be $\pm 0.02\%$.

Plutonium was determined by an amperometric titration method¹⁷ with an accuracy of ± 0.1 w/o.

Oxygen-to-metal ratio was determined gravimetrically by a standard oxidation-reduction method.¹⁸

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