

STUDY OF URANIUM-PLUTONIUM MONOXIDES

Quarterly Progress Report
Period of July 1, 1965 through September 30, 1965

Authors

United Nuclear

R. L. Forbes, N. Fuhrman

The Carborundum Company

J. Andersen, K. Taylor

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Approved: A. Strasser, Manager
Plutonium Fuels Section

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Subcontractor
THE CARBORUNDUM COMPANY
Niagara Falls, New York

Work Performed by

United Nuclear Corporation

C. Dwy
R. Forbes
N. Fuhrman
C. Johansen
A. Koehl
A. Magdics
E. Stokhamer
A. Strasser
O. Sullivan

The Carborundum Company

J. Andersen
C. Boos
T. Keaty
K. Taylor

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ABSTRACT

Uranium-plutonium monoxide-type compositions stabilized with carbon, (UPu)(OC), were synthesized by carbon reduction of mixed UO_2 and PuO_2 in helium and vacuum. Materials containing as high as 85 w/o of a (UPu)(OC) composition were produced with oxygen atom fractions as high as 0.56. Carbon-stabilized and nitrogen-stabilized uranium-plutonium monoxides, (UPu)(OCN), were synthesized by the uranium metal and carbon reduction routes in helium and vacuum. Essentially single-phase compositions were obtained having oxygen atom fractions as high as 0.36.

Specimens containing (UPu)(OCN) compositions were subjected to water corrosion tests. A material containing 91 w/o of $(\text{U}_{0.9}\text{Pu}_{0.1})(\text{O}_{0.21}\text{C}_{0.37}\text{N}_{0.42})$ was intact after exposure to boiling water for 137 hr, but it disintegrated in 550°F water.

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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 is sponsored jointly by the USAEC and Euratom. The prime contractor is the United Nuclear Corporation, Development Division, and the subcontractor is The Carborundum Company. United Nuclear is conducting fabrication studies in vacuum and is performing property determinations. Carborundum is fabricating samples in helium.

This report summarizes progress for the period of July 1, 1965 through September 30, 1965. Previous progress was reported in:

UNC-5096, Study of Uranium-Plutonium Monoxides, Progress Report, Period of February 1, 1964 through July 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).

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1. INTRODUCTION AND SUMMARY OF PRIOR RESULTS

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

The power generation limit of a given size fuel rod is directly proportional to the product of $[\text{T}_{\text{fuel center}} (\sim\text{melting}) - \text{T}_{\text{fuel surface}}] \times$ fuel thermal conductivity. A higher heat generating (high thermal conductivity) fuel will permit fewer, larger diameter rods to be used. Fewer rods will lower fuel fabrication costs. Larger diameter rods will be mechanically more stable; sizes above 1/4-in. diameter are desirable for the long fuel rods of thermal reactors (~ 10 ft).

A high conductivity uranium-plutonium monoxide fuel would be of interest to the water-cooled converter power reactor systems. Homogeneous uranium-plutonium oxide mixtures can be used with a fissionable plutonium atom enrichment of about 5 to 8% to substitute for U^{235} . This can reduce reliance on the availability of 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 in uranium would be up to 10%.

The monoxides should have high thermal conductivity, based on the similarity of their crystal and electronic structure to known high thermal conductivity monocarbides and mononitrides. Uranium monoxide is not thermodynamically stable in

massive form, but uranium-plutonium monoxide mixtures stabilized with carbon or nitrogen, or both, have been prepared in recent investigations.¹⁻³

The specific objectives of this study are: (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 diffusivity. Superior fuel compositions will be further characterized with respect to melting point, vapor pressure, and compatibility with clad materials.

Two synthesis routes are being studied: (1) reduction of the mixed dioxides (PuO_2 and UO_2) by carbon, and (2) reduction by noncarbonaceous agents, such as uranium metal. The reactions are being carried out in helium and in vacuum. The fuels are evaluated by metallography, chemical analysis, X-ray diffraction, and density measurements.

The results of work prior to this quarterly period confirmed expectations that a pure monoxide, $(\text{UPu})\text{O}$, could not be synthesized. However, essentially single-phase $(\text{UPu})(\text{OC})$ compositions could be prepared in helium and vacuum by reacting UO_2 and PuO_2 with carbon, or uranium metal with carbon stabilizer. For example, a 94% dense $(\text{UPu})(\text{OC})$ material resulted from reacting a mixture of UO_2 , PuO_2 , UH_x , and UC at 1650°C in helium. The composition was approximately 93 w/o $\text{M}(\text{O}_{0.34}\text{C}_{0.66})^*$ and 7 w/o MO_2 . Further studies indicated that the maximum oxygen atom fraction of the $\text{M}(\text{OC})$ phase in the material produced in helium was 0.58, while that in the material produced in vacuum was 0.89. However, in both cases, the fraction of the $\text{M}(\text{OC})$ phase present was low.

Attempts to synthesize a high oxygen monoxide-type material stabilized with nitrogen, i.e., a $(\text{UPu})(\text{ON})$ compound, were unsuccessful in that a single-phase prod-

*M is an abbreviation for $(\text{U}_{0.9}\text{Pu}_{0.1})$. The notation (UPu) is retained where a general class of materials is discussed.

uct did not appear possible and the oxygen solubility in the monoxide phase was low.

The synthesis of (UPu)(OCN) compounds was then undertaken in which nitrogen was substituted for some of the carbon in (UPu)(OC) to improve water corrosion resistance. A material containing 91 w/o $M(O_{0.21}C_{0.37}N_{0.42})$ was prepared reproducibly for corrosion testing by reacting a mixture of UO_2 , PuO_2 , UC, UH_x , and UN at $1650^\circ C$ in helium. This composition was virtually unaffected by a 73.5-hr exposure to boiling water. However, essentially single-phase $M(O_{0.32}C_{0.68})$ disintegrated in a boiling water corrosion test.

Preliminary room temperature thermal diffusivity measurements on M(OC) materials indicated that compositions containing as little as 50% monoxide-type phase have at least twice the thermal conductivity of UO_2 .

2. SUMMARY OF PROGRESS THIS QUARTER

The synthesis of (UPu)(OC) compositions (having intended oxygen atom fractions of 0.6 and 1.0) by carbon reduction in helium and vacuum was studied to produce single-phase materials containing high oxygen atom fractions. In the case of intended $M(O_{0.6}C_{0.4})$ synthesis in helium, it was found that the products after reaction at 1750°C contained a maximum monoxide-phase weight fraction and an oxygen atom fraction of 86 w/o and 0.38 a/o, respectively.

The synthesis of intended MO was investigated to obtain the maximum oxygen atom fraction in the (UPu)(OC) phase. Extensive ball milling of the starting materials and the use of submicron UO_2 having a particle size smaller than that employed previously did not improve upon earlier results. Although an oxygen atom fraction of 0.58 was obtained, the monoxide-phase weight fraction was only 58 w/o. The use of phenolformaldehyde resin as a substitute for the usual carbon powder reducing agent produced a material containing 85 w/o of an $M(O_{0.56}C_{0.44})$ phase in a preliminary experiment.

The synthesis of materials containing (UPu)(OCN) compositions was studied because of their apparent superior boiling water corrosion resistance. The uranium metal reduction method was employed to study the effect of the variation of the intended oxygen atom fraction with a constant intended carbon fraction of 0.2. In both helium and vacuum, monoxide-type phase weight fractions of greater than 95 w/o were obtained from reactions to synthesize intended $M(O_{0.2}C_{0.2}N_{0.6})$.

Intended $M(O_{0.5}C_{0.2}N_{0.3})$ and $M(O_{0.5}C_{0.4}N_{0.1})$ were synthesized by uranium metal reduction and sintered in vacuum. The results indicated that the use of submicron UO_2 in the reaction mixture did not increase the monoxide weight fraction of the product over the 79 w/o maximum previously obtained.

Test specimens containing (UPu)(OCN) weight fractions greater than 90 w/o were produced in a synthesis and sintering study of intended $M(O_{0.3}C_{0.3}N_{0.4})$ and $M(O_{0.3}C_{0.4}N_{0.3})$ by the uranium metal reduction in vacuum. The synthesis of these intended compositions by carbon reduction of the mixed dioxides and UN also yielded monoxide-phase weight fractions exceeding 90 w/o.

Specimens containing 91 w/o of an $M(O_{0.21}C_{0.37}N_{0.42})$ composition did not change in weight or dimensions significantly after 137 hr in boiling water. However, upon exposure to 550°F water in an autoclave this material disintegrated within 1 hr.

3. FABRICATION EXPERIMENTS

3.1 INTRODUCTION

The fabrication effort during this reporting period included the following activities:

1. The preparation of single-phase (UPu)(OC) compositions having higher oxygen atom fractions than obtained previously was studied by carbon reduction in helium and vacuum.
2. Preparation of materials containing (UPu)(OCN) compositions was continued with the objective of maximizing the weight fraction of the monoxide phase and minimizing the carbon atom fraction. Synthesis was by the uranium metal reduction route in helium and vacuum. The effect of subsequent crushing and sintering on the density and composition of the reaction products was investigated.

The intended compositions and process variables investigated under items 1 and 2 above are summarized in Table 1.

The emphasis on maximizing the oxygen atom fraction and the nitrogen atom fraction of the monoxide phase was dictated by the results of the boiling water corrosion tests conducted in the previous quarter.⁴ These showed that an oxygen atom fraction of 0.32 in essentially single-phase (UPu)(OC) was insufficient to prevent disintegration. However, good corrosion resistance was observed where

TABLE 1 — SUMMARY OF FABRICATION EXPERIMENTS

Variables Investigated	Intended Composition (Atom Fraction Range)				
	(UPu)(OC)		(UPu)(OCN)		
	<u>O_{0.6}C_{0.4}</u>	<u>O_{1.0}</u>	<u>O_{0.2/0.6}C_{0.2}N_{0.6/0.2}</u>	<u>O_{0.5}C_{0.2/0.4}N_{0.3/0.1}</u>	<u>O_{0.3/0.4}C_{0.3/0.4}N_{0.3/0.4}</u>
Synthesis conditions					
Method	Carbon reduction: 9 UO ₂ + PuO ₂ + 18 C → 10 (U _{0.9} Pu _{0.1})(O _{0.6} C _{0.4}) + 14 CO ↑		Uranium metal reduction: 5 UH _x + 3 UO ₂ + 2 UN + 8 UC + 2 PuO ₂ → 20 (U _{0.9} Pu _{0.1})(O _{0.5} C _{0.4} N _{0.1}) + 5x/2 H ₂ ↑		Uranium metal reduction Carbon reduction
Atmosphere	Helium —	Helium Vacuum	Helium Vacuum	Vacuum —	Vacuum —
Time, °C (hold time, hr)	1750 (1½ to 3)	1750 (2) 1650 (5)	1650 (5) —	1650 (5) —	1550 to 1750 (5) 1650 (5)
Blend uniformity					
Ball milling time, hr	72	24 vs 72	—	—	—
UO ₂ particle size, μ	3	0.5 vs 3	0.5	0.5	0.5
Sintering conditions					
Temp, °C (hold time, hr)	—	—	—	1650 (3)	1650 (3)
Other variables					
Form of reducing agent	—	Carbon powder vs phenolformaldehyde	—	—	—
Synthesized form	—	Granules vs pellets	—	—	—

the sum of the oxygen and nitrogen atom fractions was 0.63 in a (UPu)(OCN) composition.

As in earlier work, a uranium-plutonium ratio of 9:1 was used to represent the maximum enrichment representative of plutonium-fueled thermal reactors.

3.2 SYNTHESIS OF (UPu)(OC) COMPOSITIONS

3.2.1 Intended $(U_{0.9}Pu_{0.1})(O_{0.6}C_{0.4})$ by Carbon Reduction in Helium

Synthesis experiments to produce intended $M(O_{0.6}C_{0.4})$ by carbon reduction of the mixed dioxides in helium were conducted with the aim of obtaining compositions having substantially higher oxygen atom fractions than 0.32, which was demonstrated to be too low for water corrosion resistance. Previous studies with this intended composition involved a synthesis temperature of 1650°C which led to oxygen atom fractions no higher than 0.32.⁴ During this reporting period, the effect on composition of raising the synthesis temperature to 1750°C was investigated. In addition, to promote a more complete reaction, the starting materials were blended by ball milling for 72 hr instead of the usual 24 hr.

The synthesis conditions and the results of product characterization are shown in Table 2. The monoxide-phase weight fractions,* ranging from 82 to 86 w/o, and the oxygen atom fractions, ranging from 0.36 to 0.38, are not significantly better than those obtained from earlier carbon reduction of intended (UPu)(OC) compositions. Furthermore, these weight fractions are somewhat less than the

*The weight fraction of the monoxide phase is calculated from volume fraction data obtained by a point count technique, and from phase densities obtained by the X-ray diffraction method. The carbon atom fraction of the monoxide-type phase is calculated by assuming all the carbon in the product is in that phase. The oxygen atom fraction of the monoxide-type phase is then determined by difference.

TABLE 2 — SYNTHESIS OF INTENDED $(U_{0.9}Pu_{0.1})(O_{0.8}C_{0.4})$ BY CARBON REDUCTION OF UO_2 AND PuO_2 IN HELIUM

Exp. No.	Temp, °C (Hold Time, hr)	Material Form	Carbon Content of Reacted Product, %	Amount of M*(OC) Phase Excluding Pores, w/o	Corrected M(OC) Composition†	X-Ray Diffraction Analysis	
						Phase Intensity	Lattice Parameter
1	1750 (1½)	Wafer, <1/16-in. thick × 1/4-in. diameter	2.48	82	M(O _{0.37} C _{0.63})	Strong M(OC)	4.9573 ± 0.0009
						Strong MO _{2-x}	5.4770 ± 0.0005
2	1750 (3)	Wafer, <1/16-in. thick × 1/4-in. diameter	2.49	84	M(O _{0.38} C _{0.62})	Strong M(OC)	4.9567 ± 0.0005
						Strong MO _{2-x}	5.4781 ± 0.0011
3	1750 (2)	Pellet, 1/4-in. thick × 1/4-in. diameter	2.52	83	M(O _{0.38} C _{0.64})	Strong M(OC)	4.9585 ± 0.0009
						Strong MO _{2-x}	—
4	1750 (2)‡	Pellet, 1/4-in. thick × 1/4-in. diameter	2.57	86	M(O _{0.38} C _{0.62})	Strong M(OC)	4.9565 ± 0.0004
						Strong MO _{2-x}	—

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

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

‡Quenched from 1750°C to below red heat in about 10 seconds.

92 w/o minimum achieved previously with intended $M(O_{0.5}C_{0.5})$.⁴ On the basis of these results, no further synthesis of intended $M(O_{0.6}C_{0.4})$ is planned.

3.2.2 Intended $(U_{0.9}Pu_{0.1})O$ by Carbon Reduction in Helium

To produce materials with higher oxygen atom fractions in the $(UPu)(OC)$ 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 atom fractions as high as 0.58.⁵ The effort this quarter to improve upon this result involved investigations 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 3 under Experiments 1 and 2 show no substantial improvement in monoxide-phase weight fraction and oxygen atom fraction 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 3 for the

TABLE 3 — SYNTHESIS OF INTENDED ($U_{0.9}Pu_{0.1}$)O BY CARBON REDUCTION OF UO_2 AND PuO_2 AT 1750°C FOR 2 HR

Exp. No.	Ball Milling Time, hr	Material Form	Amount of $M^*(OC)$ Phase Excluding Pores, w/o	Corrected $M(OC)$ Composition†	X-Ray Diffraction Analysis, Phases Present, and Lattice Parameter, Å	
					$M(OC)$	MO_{2-x}
1	72	Granulated	58	$M(O_{0.58}C_{0.42})$	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

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

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

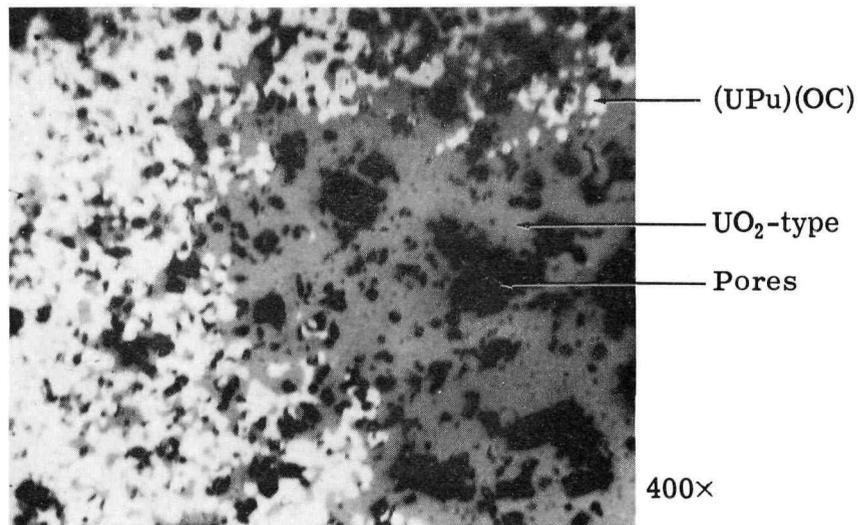
‡Prepared with 0.5-micron UO_2 powder. The usual 3-micron UO_2 powder was used in the other experiments.

two UO_2 starting materials (Experiments 3 and 4) indicate that the products of synthesis at 1750°C were similar.

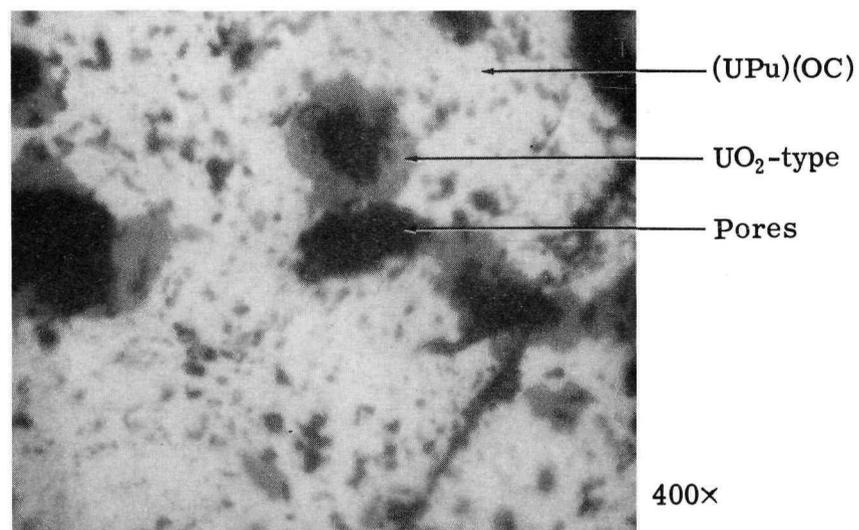
Metallographic examination of the intended MO synthesis products revealed segregation of the $\text{M}(\text{OC})$ and MO_{2-x} phases (see Fig. 1a). Therefore, an attempt was made to improve the reaction blend uniformity by substituting liquid phenol-formaldehyde resin for the powdered carbon normally 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 necessary 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, atmosphere, etc. 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 $\text{M}(\text{O}_{0.56}\text{C}_{0.44})$ phase. X-ray diffraction analysis indicated the usual MO_{2-x} phase ($a_0 = 5.4832 \pm 0.0020 \text{ \AA}$), and a strong $\text{M}(\text{OC})$ 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. 1b) and although the oxygen atom fraction has not been significantly increased, this technique promises to yield higher weight fractions of the high oxygen $\text{M}(\text{OC})$ than previously obtained. Further development is required, however, to optimize the process.



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



b. Improved distribution after substituting phenolformaldehyde for carbon powder

Fig. 1 — 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

3.2.3 Intended (U_{0.9}Pu_{0.1})O by Carbon Reduction in Vacuum

In previous work,⁵ the most promising product of an intended MO synthesis by carbon reduction in vacuum contained 60 w/o of an M(O_{0.60}C_{0.40}) phase. During this quarter, the effect of using the 0.5-micron particle size UO₂ was investigated. It was expected that this relatively fine starting material would blend more efficiently with the PuO₂ and C, react more completely, and, therefore, produce more nearly single-phase (UPu)(OC) with a higher oxygen atom fraction.

The starting materials were blended in a 3-ml Spex* mill for 1 hr and were compacted without binder at forming pressures of 15,000, 30,000, and 60,000 psi. Compacts representing the three pressing conditions were heated at 1650°C for 5 hr. A preliminary evaluation indicated that the compacts pressed at 30,000 psi produced the maximum monoxide weight fraction. The reproducibility of the process was checked by a second run. A complete metallographic examination of the two synthesis products showed that they were similar; but, in both cases, large cracks were found around which an MO_{2-x} phase was concentrated. Because monoxide-phase weight fraction and oxygen atom fraction data obtained from such inhomogeneous structures by the usual point count technique are believed unreliable, the synthesis products were analyzed by X-ray diffraction. Although quantitative weight fraction data cannot be obtained from this analysis, the oxygen atom fraction of the M(OC) phase can be estimated fairly accurately by comparison of the indicated lattice parameter with the lattice parameter-oxygen atom fraction correlation developed previously for M(OC) compositions (see Fig. 2). The lattice parameters of $4.9523 \pm 0.0006 \text{ \AA}$ and $4.9528 \pm 0.0007 \text{ \AA}$ for the M(OC) type phases of the two synthesis products correspond to an oxygen atom fraction of approximately 0.6.

This is not significantly different from the best values obtained with the 3-micron UO₂ starting material so that there is no obvious advantage in using the submicron

*A commercial oscillating shaker made by Spex Industries.

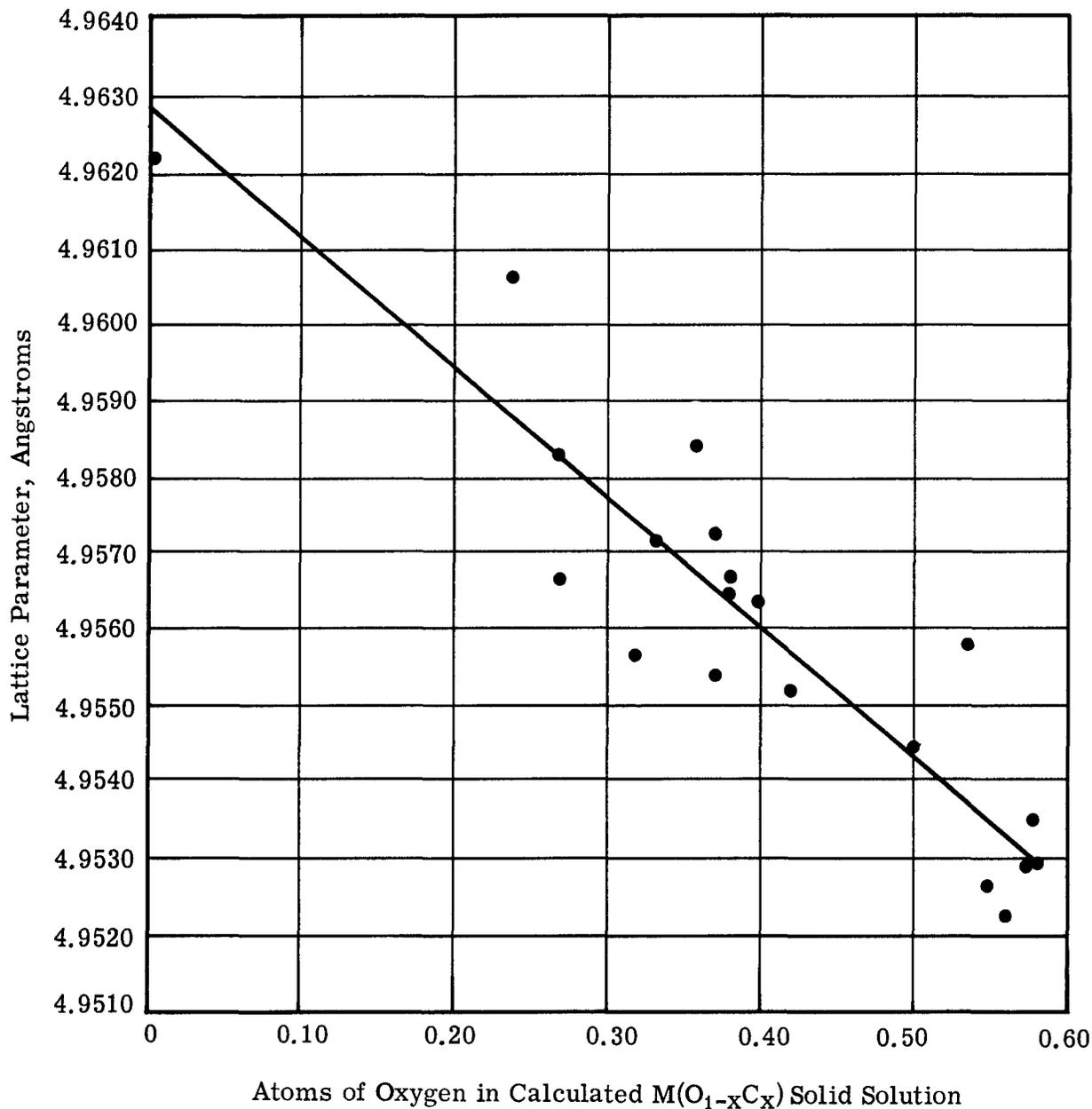


Fig. 2 — Variation of Lattice Parameter of the M(O_{1-x}C_x)Phase with Oxygen Content. Carbon Reduction of UO₂ and PuO₂ at 1750°C.

UO₂. The oxygen atom fraction is in good agreement with those obtained from intended MO synthesis by the standard carbon reduction in helium.

3.3 SYNTHESIS OF (UPu)(OCN) COMPOSITIONS

3.3.1 Intended (U_{0.9}Pu_{0.1})(O_xC_{0.2}N_{0.8-x}) by Uranium Metal Reduction in Helium

The objective of synthesizing M(OCN) compositions by uranium metal reduction was to make an essentially single-phase product with superior stability in high temperature water. Previous boiling water corrosion tests indicated that monoxide-type materials with minimal carbon content would have the best corrosion resistance. Therefore, an effort in this reporting period involved intended compositions with the carbon atom fraction fixed at 0.2. The intended oxygen and nitrogen atom fractions were varied from 0.2 to 0.6, as shown in Table 3.

The reaction mixtures were blended for 30 minutes in a 25-ml Spex mixer, pressed into 1/4-in. diameter pellets, and heated for 5 hr at 1650°C in a tantalum-lined graphite crucible with a helium flow of 6 ft³/hr. The results in Table 4 indicate that the product metal content decreases and the monoxide weight fraction increases with decreasing intended oxygen. On the basis of these data the product of the intended M(O_{0.2}C_{0.2}N_{0.6}) synthesis was deemed sufficiently promising for water corrosion testing. The last experiment in Table 4 presents the characterization data on a sample representing 12 specimens fabricated for such tests. A comparison with the data on the original synthesis product demonstrates the good reproducibility of the fabrication process.

3.3.2 Intended (UPu)(OCN) by Uranium Metal Reduction in Vacuum

A. Intended M(O_xC_{0.2}N_{0.8-x}) Compositions

In view of the favorable helium atmosphere results described in Section 3.3.1, three compositions with intended carbon atom fractions of 0.2 were synthesized

TABLE 4 — 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			Corrected M(OCN) Composition†	M(OCN) Lattice Parameter, Å
	M(OCN)	MO_{2-x}	Metal		
$M(O_{0.6}C_{0.2}N_{0.2})$	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	—	$M(O_{0.10}C_{0.28}N_{0.62})$	—

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

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

‡Pellets for water corrosion tests.

by uranium metal reduction in vacuum: $M(O_{0.2}C_{0.2}N_{0.6})$, $M(O_{0.3}C_{0.2}N_{0.5})$, and $M(O_{0.4}C_{0.2}N_{0.4})$. Compacts of the blended starting materials were prepared in the usual manner and heated at 1650°C for 5 hr. The characterization data on these products are summarized in Table 5. As in the case of the helium atmosphere work, an essentially single-phase material was produced from the intended $M(O_{0.2}C_{0.2}N_{0.6})$ synthesis.

B. Intended $M(O_{0.5}C_yN_{0.5-y})$ Compositions

At the beginning of the reporting period, several syntheses by uranium metal reduction in vacuum were conducted to reproduce two promising M(OCN) materials resulting from the previous quarter's survey in which the intended oxygen atom fraction ranged from 0.5 to 0.8.⁴ These contained the highest monoxide-phase weight fractions found: 77 w/o of $M(O_{0.38}C_{0.45}N_{0.19})$ 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.

TABLE 5 — SYNTHESIS OF INTENDED $(U_{0.9}Pu_{0.1})(O_xC_{0.2}N_{0.8-x})$ BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC AND UN IN VACUUM AT 1650°C FOR 5 HR

Exp. No.	Intended Composition*	Carbon Content, w/o			Nitrogen Content, w/o			Metallographic Results, Phases Present, and Amount, w/o			Corrected M(OCN) Composition†	Density, g/cm ³
		Total Intended	Total Actual	Contained in M(OCN)	Total Intended	Total Actual	Contained in M(OCN)	M(OCN)	MO _{2-x}	Metal		
83	M(O _{0.2} C _{0.2} N _{0.8})	0.95	0.96	0.99	3.33	4.05	4.18	97	3	—	M(O _{0.04} C _{0.21} N _{0.75})	11.1
84	M(O _{0.3} C _{0.2} N _{0.5})	0.95	0.93	0.98	2.77	3.50	4.08	86	9	5	M(O _{0.05} C _{0.22} N _{0.73})	10.6
85	M(O _{0.4} C _{0.2} N _{0.4})	0.95	0.97	1.19	2.22	2.86	3.51	81	19	—	M(O _{0.13} C _{0.25} N _{0.62})	11.3

*M = (U_{0.9}Pu_{0.1}).

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

The 0.5-micron UO_2 was employed during this reporting period (previous work used 3-micron UO_2) to obtain more uniform blends and, hopefully, higher M(OCN) weight fractions. Several reaction mixes of UH_x , UO_2 , PuO_2 , UN, and UC formulated to produce intended $\text{M}(\text{O}_{0.5}\text{C}_{0.4}\text{N}_{0.1})$ and $\text{M}(\text{O}_{0.5}\text{C}_{0.2}\text{N}_{0.3})$ were blended, compacted at 30,000 psi, heated to 1650°C, and held for 5 hr during synthesis.

The results of the experiments are summarized in Table 6, which also includes the previous synthesis results for comparison (Experiments 50 and 51).

Although good reproducibility was achieved in the case of the intended $\text{M}(\text{O}_{0.5}\text{C}_{0.4}\text{N}_{0.1})$ synthesis, the presence of the undesirable metal phase ruled out further work on this composition.

The products from the intended $\text{M}(\text{O}_{0.5}\text{C}_{0.2}\text{N}_{0.3})$ syntheses (Experiments 63 and 65) exhibited widely varying oxygen atom fractions ranging from 0.09 to 0.29, as compared with 0.20 for the original run (Experiment 50). In addition, these materials were relatively porous. To increase their density, the synthesis products were crushed, repressed, and sintered. The Table 6 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 atom fraction of the monoxide-type phase. Although it appeared that additional development was required to obtain an equilibrium product stable at 1650°C in vacuum, this work was discontinued because the attainment of a single-phase M(OCN) composition with O/C ratios of 5/2 did not seem possible.

C. Intended $\text{M}(\text{O}_{0.3}\text{C}_y\text{N}_{0.7-y})$ Compositions

Helium atmosphere syntheses of intended $\text{M}(\text{O}_{0.3}\text{C}_{0.3}\text{N}_{0.4})$ and $\text{M}(\text{O}_{0.3}\text{C}_{0.4}\text{N}_{0.3})$ by uranium metal reduction had yielded nearly single-phase M(OCN) in previous work.⁴ 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

TABLE 6 — 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 (Total Hold Time, hr)	Carbon Content, w/o			Nitrogen Content, w/o			Metallographic Results, Phases Present, and Amount, w/o			Corrected M(OCN) Composition†	Density, g/cm ³	Remarks
			Total Intended	Total Actual	Contained in M(OCN)	Total Intended	Total Actual	Contained in M(OCN)	M(OCN)	MO _{2-x}	Metal			
51‡	M(O _{0.5} C _{0.4} N _{0.1})	1650 (5)	1.90	1.64	2.14	0.55	0.85	1.11	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)	1.90	1.67	2.12	0.55	0.64	0.81	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)	0.95	1.01	1.27	1.66	2.32	2.93	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)	0.95	1.12	1.60	1.66	2.25	3.22	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)	0.95	0.92	1.28	1.66	2.28	3.16	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)	0.95	1.00	1.28	1.66	2.12	2.71	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)	0.95	1.02	1.39	1.66	1.74	2.37	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)	0.95	0.99	1.41	1.66	1.75	2.49	70	30	—	M(O _{0.26} C _{0.30} N _{0.44})	12.2	Sintering crushed product of Exp. No. 65

*M = (U_{0.9}Pu_{0.1}).

†Previous results from Reference 4 using 3-micron UO₂ starting material.

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

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 7 and 8, 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, weight losses were small and the weight fractions and the oxygen atom fractions of the monoxide phases were at least as high as obtained from higher temperature syntheses. The synthesis product densities, however, were relatively low. Invariably, a density improvement was achieved by sintering the crushed synthesis products. An example is illustrated in Fig. 3. Such dense structures are preferred for water corrosion tests.

3.3.3 Intended (UPu)(OCN) by Carbon Reduction in Vacuum

The initial synthesis survey by carbon reduction in vacuum involved intended oxygen atom fractions of 0.5 to 0.8 and produced M(OCN) weight fractions as high as 78 w/o.⁴ During this reporting period, higher weight fractions were sought by synthesis of the following intended compositions using this method: $M(O_{0.4}C_{0.3}N_{0.3})$, $M(O_{0.3}C_{0.4}N_{0.3})$, and $M(O_{0.3}C_{0.3}N_{0.4})$. The starting materials (C, PuO₂, UO₂, and UN) were blended, compacted, heated to 1650°C and held for 5 hr.

The results of product characterization are shown in Table 9. The data show that M(OCN)-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. Water corrosion testing of all these materials is planned for the next reporting period.

TABLE 7 — 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 (Total Hold Time, hr)	Carbon Content, w/o			Nitrogen Content, w/o			Metallographic Results, Phases Present, and Amount, w/o			Corrected M(OCN) Composition†	Density, g/cm ³	Remarks
		Total Intended	Total Actual	Contained in M(OCN)*	Total Intended	Total Actual	Contained in M(OCN)	M(OCN)	MO _{2-X}	Metal			
73	1750 (5)	1.43	1.38	1.46	2.22	2.77	2.94	94	6	—	M(O _{0.17} C _{0.30} N _{0.53})	12.0	8% weight loss
71	1650 (5)	1.43	1.46	1.63	2.22	2.63	2.94	90	9	1	M(O _{0.13} C _{0.34} N _{0.53})	10.4	2% weight loss
69	1650 (5)	1.43	1.34	1.53	2.22	2.06	2.35	88	12	—	M(O _{0.27} C _{0.31} N _{0.42})	13.2	—
75	1620 (5)	1.43	1.46	1.80	2.22	2.51	3.10	81	17	2	M(O _{0.06} C _{0.38} N _{0.56})	11.5	1.5% weight loss
77	1550 (5)	1.43	1.50	1.56	2.22	2.34	2.44	96	4	—	M(O _{0.24} C _{0.32} N _{0.44})	11.5	1.1% weight loss
77A	1650 (3)	1.43	1.43	1.53	2.22	1.70	1.82	93	7	—	M(O _{0.36} C _{0.32} N _{0.32})	11.3	Sintering of Exp. No. 77 product

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

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

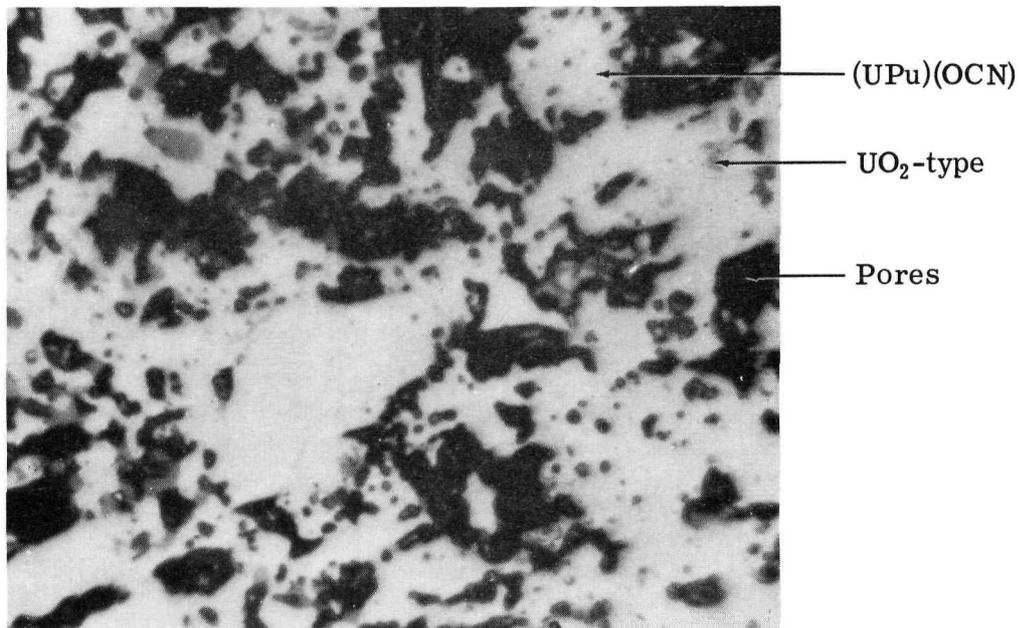
TABLE 8 — SYNTHESIS AND SINTERING OF INTENDED $(U_{0.9}Pu_{0.1})(O_{0.3}C_{0.4}N_{0.3})$ BY URANIUM METAL REDUCTION OF UO_2 AND PuO_2 WITH UC AND UN IN VACUUM

Exp. No.	Temp, °C (Total Hold Time, hr)	Carbon Content, w/o			Nitrogen Content, w/o			Metallographic Results, Phases Present, and Amount, w/o			Corrected M(OCN) Composition†	Density, g/cm ³	Remarks
		Total Intended	Total Actual	Contained in M(OCN)*	Total Intended	Total Actual	Contained in M(OCN)	M(OCN)	MO _{2-x}	Metal			
74	1750 (5)	1.90	1.22	1.28	1.67	2.28	2.39	96	1	3	M(O _{0.31} C _{0.27} N _{0.42})	12.5	33% weight loss
72	1650 (5)	1.90	1.98	2.13	1.67	1.73	1.89	93	7	—	M(O _{0.22} C _{0.45} N _{0.33})	10.9	3% weight loss
72A	1650 (3)	1.90	1.78	1.93	1.67	1.84	2.00	92	8	—	M(O _{0.23} C _{0.41} N _{0.38})	13.0	Sintering of Exp. No. 72 product
70	1650 (5)	1.90	2.00	2.19	1.67	1.73	1.89	91	9	—	M(O _{0.21} C _{0.45} N _{0.34})	13.2	—
76	1620 (5)	1.90	1.93	2.44	1.67	1.74	2.20	79	21	—	M(O _{0.08} C _{0.52} N _{0.40})	11.4	2% weight loss
76A	1650 (3)	1.90	1.94	2.04	1.67	1.78	1.87	95	5	—	M(O _{0.24} C _{0.43} N _{0.33})	12.5	Sintering of Exp. No. 76 product
78	1550 (5)	1.90	1.94	2.09	1.67	1.75	1.89	93	7	—	M(O _{0.23} C _{0.43} N _{0.34})	11.3	1.4% weight loss
78A	1650 (3)	1.90	1.82	1.94	1.67	1.65	1.76	94	5	1	M(O _{0.28} C _{0.41} N _{0.31})	11.7	Sintering of Exp. No. 78 product
79	1550 (5)	1.90	1.93	2.00	1.67	1.70	1.76	96	4	—	M(O _{0.27} C _{0.42} N _{0.31})	—	—
79A	1650 (3)	1.90	1.85	1.98	1.67	1.69	1.82	93	7	—	M(O _{0.20} C _{0.42} N _{0.38})	11.4‡	Sintering of Exp. No. 79 product

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

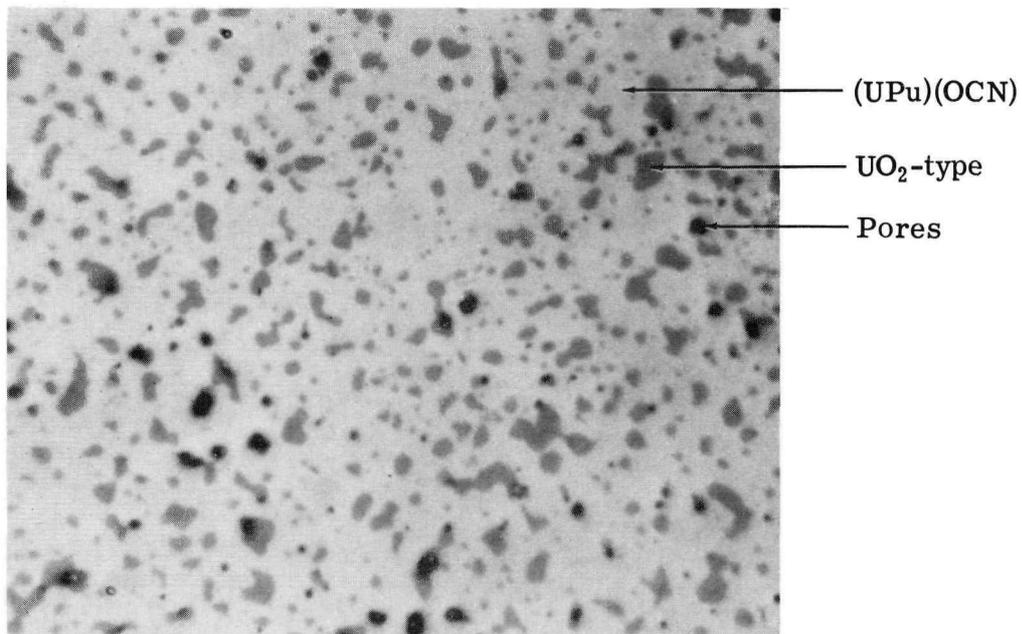
†Composition calculated from point count, carbon and nitrogen content, and assumed X-ray density.

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



520×

Synthesis Product



520×

Sintered Product

Fig. 3 — Density Improvement on Sintering Intended
($U_{0.9}Pu_{0.1}$)($O_{0.3}C_{0.4}N_{0.3}$) Synthesis Product
(Table 6, Exp. Nos. 72 and 72A)

TABLE 9 — SYNTHESIS OF (UPu)(OCN) BY CARBON REDUCTION OF UO₂ AND PuO₂ WITH UN IN VACUUM AT 1650°C FOR 5 HR

Exp. No.	Intended Compositions*	Carbon Content, w/o			Nitrogen Content, w/o			Metallographic Results, Phases Present, and Amount, w/o			Corrected M(OCN) Composition†	Density, g/cm ³
		Total Intended	Total Actual	Contained in M(OCN)	Total Intended	Total Actual	Contained in M(OCN)	M(OCN)	MO _{2-x}	Metal		
80	M(O _{0.4} C _{0.3} N _{0.3})	1.43	1.88	2.13	1.66	1.49	1.69	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})	1.43	1.81	1.97	2.22	1.88	2.04	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})	1.90	2.17	2.24	1.67	1.47	1.52	97	3	—	M(O _{0.26} C _{0.48} N _{0.26})	9.7

*M = (U_{0.9}Pu_{0.1}).

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

4. FUEL EVALUATION

4.1 INTRODUCTION

Promising materials consisting of essentially single-phase compositions of M(OCN) were screened by corrosion testing in boiling water. Specimens of materials which survived the test were exposed to 550°F water in an autoclave. (UPu)O₂ pellets will be tested under similar conditions for comparison.

Thermal diffusivity measurements are planned for those compositions exhibiting superior water corrosion resistance.

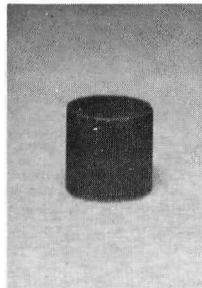
4.2 WATER CORROSION

4.2.1 Boiling Water Tests

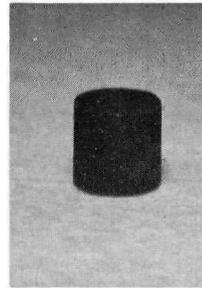
Corrosion testing of specimens containing 91 w/o M(O_{0.21}C_{0.37}N_{0.42}) was continued during this reporting period. A boiling water test was conducted on two pellets to check the reproducibility of the good corrosion resistance observed in the previous 73.5-hr test of this material.⁴ The pellets were immersed in separate flasks of boiling distilled water located in a nitrogen atmosphere glove box. The weight and dimensional changes found after 137 hr are small, and they are presented in Table 10. Photographs of a pellet before and after the test are shown in Fig. 4. As in the previous test, the pellets changed color from grey to black and a small amount of material spalled off each pellet. This residue was recovered and in

TABLE 10 — CORROSION DATA ON
 $(U_{0.9}Pu_{0.1})(O_{0.21}C_{0.37}N_{0.42})$ AFTER 137 HR IN
 BOILING WATER

	<u>Pellet Number</u>	
	<u>2</u>	<u>4</u>
Weight Change		
Grams	-0.0028	-0.0030
Per cent of original weight	-0.26	-0.28
Diameter Change		
Inches	+0.0004	-0.0001
Per cent of original diameter	+0.21	-0.05
Height Change		
Inches	+0.0001	-0.0001
Per cent of original height	+0.05	-0.05



a. Before exposure



b. After exposure

Fig. 4 — 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

each case it weighed 4 mg. These data are in substantial agreement with those obtained from the earlier test.

A boiling water test was also initiated on the $M(O_{0.10}C_{0.28}N_{0.62})$ composition which was prepared during this quarter by uranium metal reduction in helium. After a 24-hr exposure, a negligible weight change was observed. Further testing of this material in boiling water is planned.

4.2.2 Autoclave Tests

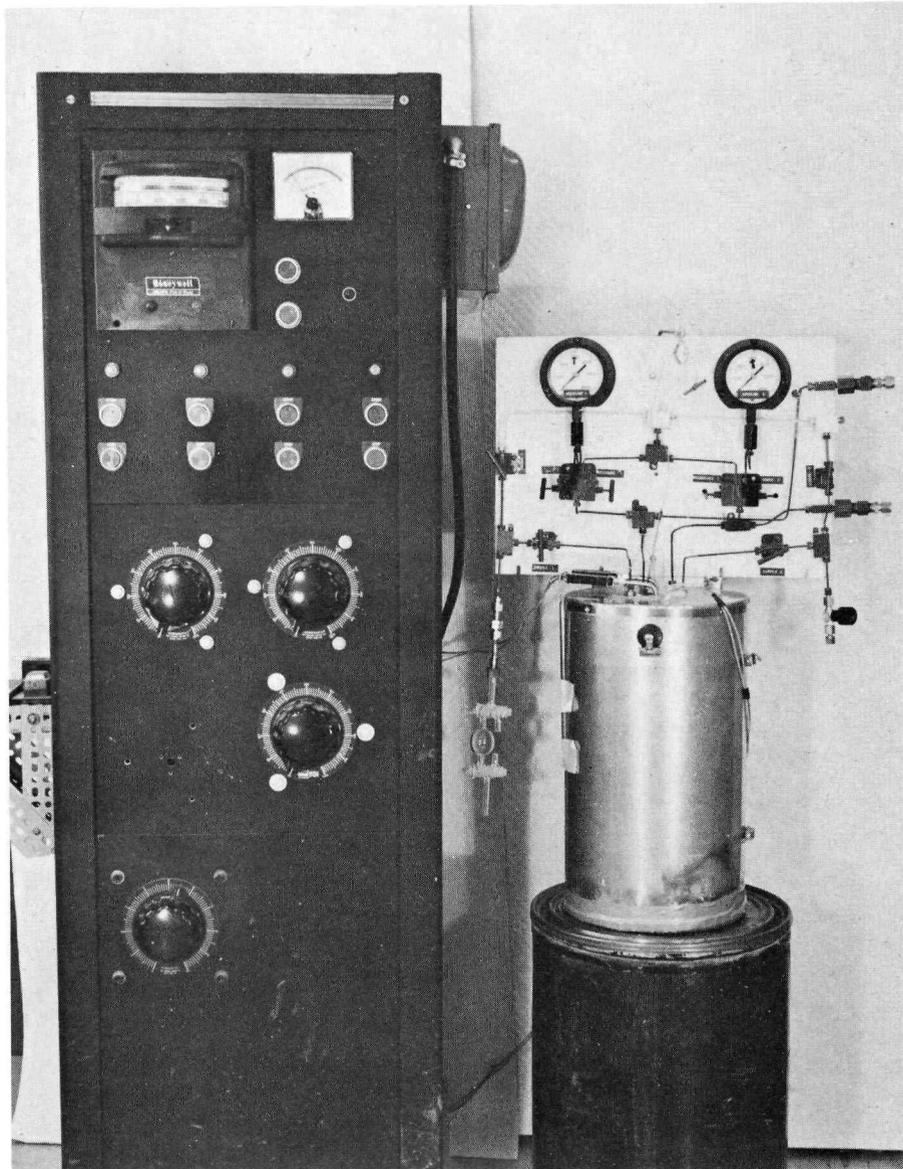
In preparation for testing in high temperature water, the autoclave furnace and piping, shown in Fig. 5, were installed in a nitrogen atmosphere glove box. Two autoclaves (Kuentzel bombs), each of approximately 100-ml capacity, are heated simultaneously by the furnace. Prior to installation a testing procedure was established to assure that a satisfactory test in deoxygenated water would be conducted in the glove box. Preliminary experiments indicated that an oxygen level of 0.2 ppm or less is achieved by bleeding off steam with the autoclave temperature maintained above 212°F. The modified spectrophotometric Winkler method* was employed to determine the oxygen level in the water.

Autoclave corrosion tests in 550°F water were conducted on four specimens containing 91 w/o $M(O_{0.21}C_{0.37}N_{0.42})$. Initially, two specimens (one per autoclave) were tested in distilled deaerated water for 4 hr. Upon completion of the test, both specimens were found disintegrated. Two additional specimens were then exposed for 1 hr to 550°F water with the same unfavorable results. The finely divided hydrolysis product from these tests was recovered and is being characterized by X-ray diffraction analysis.

4.3 THERMAL DIFFUSIVITY

No thermal diffusivity measurements were performed during this quarter.

*Procedure published in ORNL Master Analytical Manual.



Neg. No. 4783

Fig. 5 — View of Autoclave Furnace, Piping, and Control Panel

5. CONCLUSIONS

The major conclusions derived from the work this quarter are:

1. Although nearly single-phase (UPu)(OC) compositions can be obtained reproducibly from the synthesis of intended $M(O_{0.6}C_{0.4})$ by carbon reduction of the mixed dioxides in helium, the maximum oxygen atom fraction in the monoxide is no greater than the approximately 0.4 found in previously produced single-phase material.
2. Higher oxygen atom fractions (approaching 0.6) can be produced by the standard carbon reduction route; however, the weight fraction of the monoxide is limited to approximately 60 w/o. The use of phenolformaldehyde resin in place of carbon powder as the reducing agent promises to increase the monoxide weight fraction.
3. The substitution of a submicron UO_2 for the usual 3-micron starting material does not significantly affect the M(OC)-phase weight fraction or oxygen atom fraction resulting from carbon reduction syntheses.
4. The synthesis studies of various (UPu)(OCN) materials employing the uranium metal and carbon reduction methods indicate that monoxide-phase weight fractions of 90 w/o or greater are obtained when the intended oxygen atom fraction is restricted to a maximum of 0.3 and the intended oxygen to carbon atom ratio is no more than 1.
5. In the essentially single-phase M(OCN) compositions produced, the sum of the oxygen and nitrogen atom fractions actually found is generally in

good agreement with the intended composition.

6. Synthesis of M(OCN) compositions by uranium metal reduction in vacuum at 1750°C is accompanied by a high vaporization rate. Lower synthesis temperatures (1550 to 1650°C) produced essentially equivalent materials without significant weight loss.
7. Although a monoxide type material containing 91 w/o M(O_{0.21}C_{0.37}N_{0.42}) withstood exposure to boiling water for 137 hr, it disintegrated within 1 hr in 550°F water.

6. WORK PLANNED FOR NEXT QUARTER

During the next quarter, the fabrication of test specimens will be completed. Boiling water and autoclave corrosion tests will be performed on the most promising M(OC) and M(OCN) materials produced to date. Thermal diffusivity measurements will be made on selected compositions. Similar tests will also be performed on $(UPu)O_2$ for comparison.

7. REFERENCES

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