THE CARBOTHERMIC SYNTHESIS OF A MIXED
 URANIUM-PLUTONIUM NITRIDE

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ABSTRACT

The synthesis of solid solution uranium-plutonium nitride from a mixture of uranium dioxide, plutonium dioxide and carbon in an atmosphere of nitrogen is described. The general reaction $0.80 \text{ UO}_2 + 0.20 \text{ PuO}_2 + 2 \text{ C(s)} + 1/2 \text{ N}_2(\text{g}) \rightleftharpoons (\text{U}_{0.80}\text{Pu}_{0.20})\text{N} + 2\text{CO(g)}$ was carried out at 1600°C with a brief test of completeness at 1700°C. Carbon was added in slight excess to increase the ratio of conversion and, following synthesis, steps were taken to remove the excess. The carbothermic reaction was carried out in a particle-bed reactor under a continuous and constant nitrogen flowrate. Kinetics for the reaction under synthesis conditions were followed by monitoring the reaction offgas for carbon monoxide. Rate constants at several temperatures between 1430 and 1625°C were determined. Total reaction time for a 50 gram batch was about 4 to 5 hours with approximately 99.6% of the oxide being reduced.

A standard mixed-nitride composition that has been reproducibly synthesized is:

U/Pu Ratio	- 4.0
N	- 5.30 wt. %
C	- 0.20 wt. %
O	- 0.10 wt. %
Lattice Parameter	- 4.893 Å

I. INTRODUCTION

Direct synthesis of mixed uranium-plutonium mononitride from the individual oxides is possible using the carbothermic reaction. This reaction presents an alternative to present mixed-nitride production methods using mostly metal or metal-hydride starting materials. The economic potential of carbothermic fuel material as compared with metal-derived materials has been calculated by Fletcher and Greenborg⁽¹⁾ for a model carbide breeder reactor. The calculations indicate that a carbothermic process such as described in this paper could provide nitrides at a cost nearly comparable with other fast reactor fuels if present purity levels are found acceptable.

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II. Discussion of the Carbothermic Reaction and Related Work

The general nitride carbothermic reaction is

$$\text{MO}_2 + 2\text{C} + 1/2 \text{N}_2(\text{g}) \rightleftharpoons \text{MN} + 2 \text{CO}(\text{g}). \quad \text{M} = \text{U, Pu or UPu}.$$

The reaction has been studied by a number of investigators: Hyde and et al⁽²⁾, Gens⁽³⁾, Gens, Helton and Clinton⁽⁴⁾, Imoto and Stöcker⁽⁵⁾ and very recently by McLaren, Dicker, Harrison and Russell⁽⁶⁾. British researchers Hyde and company, and McLaren and coworkers have used the reaction to prepare uranium nitride material but complete elimination of the oxide reactant was not achieved. Gens and coworkers prepared dense uranium nitride microspheres using a sol-gel technique, and Gens and also Imoto and Stöcker published a thermodynamic treatment of the nitride carbothermic reaction.

In related work Hansen⁽⁷⁾ and Brandè and Murbach⁽⁸⁾ studied the uranium carbide-nitride conversion reaction $2 \text{UC} + 3/2 \text{N}_2(\text{g}) \rightleftharpoons \text{U}_2\text{N}_3 + 2\text{C}$. The reaction was used in a reprocessing scheme for uranium carbides and would undoubtedly be unsuitable for a nitride synthesis since a mole of carbon is produced for each mole of carbide converted.

However, even though the carbide-nitride conversion reaction doesn't provide an alternative synthesis method, it does provide a means of removing small quantities of carbide type impurities from nitride material. Use of this reaction, followed by a hydrogen reduction of the free carbon was found useful as a purification scheme. Accordingly, a synthesis process using the general carbothermic reaction, the carbide-nitride reaction and hydrogen reductions was devised and the utility of proposed process steps was verified by direct chemical analysis and lattice parameter measurements.

III. The Carbothermic-Nitride Synthesis Process

The process feed material is prepared as 10 to 15 mil diameter oxide particles containing approximately 8.7 wt. % carbon in either graphite or carbon black form. The particle feed is loaded in a tungsten particle bed reactor of special design and the synthesis is carried out in the following manner:

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1. The feed particles are reacted at temperatures up to 1700°C in flowing nitrogen according to the reaction shown. Nitrogen flow rates used in this stage are equal to or greater than 40 cc/min/gm (reactant). The reaction is continued until evolution of carbon monoxide ceases; the reaction takes about four to five hours and results in approximately 99.6% of the oxide being converted.

2. Unreacted or excess carbon is removed from the product by reducing the temperature to 1200°C and flowing hydrogen through the bed at a rate of 80 cc/min/gm (reactant). The reaction

takes two to three hours and is continued until evolution of methane ceases.

3. The chemically combined carbon is displaced from a carbonitride solid solution by reaction with nitrogen at 1200°C. The brief reaction (1 to 2 hours) yields a higher nitride plus free carbon.

4. The displaced carbon is removed by an additional hydrogen reaction cycle similar to "2" above.

5. The higher uranium nitrides formed in step "3" are decomposed by a brief outgas cycle at 1600°C in flowing helium.

The product of the five-step process is solid solution uranium-plutonium nitride. The particles are low density, homogeneous and grey in color. The particle size is approximately that of the starting material. Figure 1 shows the appearance of the nitride particles as recovered from the reactor.

The composition of a "standard" mixed nitride of U/Pu ratio 4.00 is 5.30 wt. % nitrogen, 0.20 wt. % carbon, and 0.10 wt. % oxygen. The reproducibility of this composition from batch to batch is within 0.06 wt. % units, as indicated by the data for three successive runs given in Table I. Crystal lattice parameters for the primary phase in these

compositions are uniform to within 0.001 angstrom units.

TABLE I
COMPOSITION DATA FOR SEVERAL MIXED NITRIDES
SYNTHESIZED BY CARBOTHERMIC REDUCTION

Run	UPCN-4	UPCN-6	UPCN-7
Date of Run	1/3/68	1/17/68	1/22/68
N ₂	5.22 wt. %	5.30 wt. %	5.38 wt. %
O ₂	0.10 wt. %	0.08 wt. %	0.19 wt. %
C	0.17 wt. %	0.18 wt. %	0.22 wt. %
U/Pu	4.0	4.0	4.0
Lattice Parameter	4.893 Å	4.893 Å	4.893 Å

IV. The Reaction Apparatus

The glove box synthesis apparatus and system used is illustrated in Figure 2. It consists of the tungsten gas-solid reactor supported vertically in an Astro* graphite resistance furnace, temperature monitoring and controlling devices, a reaction gas supply and purification system, reaction gas oxygen and water analyzers made by Westinghouse** and C.E.C.†, respectively, and Liratt†† type carbon monoxide and methane exhaust gas analyzers. The reaction gas having 3 ppm or less oxygen and water is passed up through the particle bed at a flow of approximately 40 cc/min/gm (reactant) and exhausts out the cap through either the carbon monoxide or the methane monitor. The reaction vessel, formed to our design by General Electric Corporation and shown in Figure 3 and 4, features a 1-7/8" diameter, electron beam machined bed support having approximately 250, 2 to 5 mil diameter holes for area-wide gas distribution. The vessel is made entirely of tungsten and can withstand thermal cycling and carbonaceous atmospheres of nitrogen, helium and hydrogen up to 1700°C. The vessel is lightly sealed with a tapered cap having an exhaust tube out the top. Capacity of the system has not been fully evaluated but fifty gram batches have routinely been processed with a total synthesis time of 16 to 20 hours.

*Astro Industries, Santa Barbara, California, Model 1000B Furnace.

**Westinghouse Electric Company, Scientific Equipment Department, Pittsburgh, Pa., Model 207L Oxygen Gauge.

†Consolidated Electrodynamic Corporation, Analytical & Control Division, Pasadena, California, Model 303 Moisture Monitor.

††Mine Safety Appliance Company, Pittsburgh, Pa., Model 300 Lira CO Analyzer, Model 300 Lira CH₄ Analyzer.

V. Reaction Kinetics

The kinetics for the carbothermic reaction in flowing nitrogen are tabulated in Table II. The reaction was observed to be first order with regards to the reactants at a nitrogen pressure of 0.98 to 1.00 atms. Rate constants for the 4:1 uranium-plutonium mixture at five different temperatures between 1430°C and 1625° were found to vary in an Arrhenius manner as shown in Figure 5. The "apparent" Arrhenius constant evaluated for the curve was 54 ± 4 kcal/mole for the nitrogen flowrate of 100 ± 5 cc/min/gm and the rate constant predicted at 1600°C from this curve was 0.023/min. During actual production runs at 1600°C under a nitrogen flowrate of 40 ± 5 cc/min/gm, the rate constants averaged 0.015/min. Pickles⁽⁹⁾ investigated the carbothermic reaction $(U_{0.85}Pu_{0.15})O_2 + 3C \rightleftharpoons (U_{0.85}Pu_{0.15})C + 2CO(g)$ under vacuum conditions and observed first order reaction kinetics and rate constants of 3.14×10^{-2} /min at 1400°C and 7.68×10^{-2} /min at 1600°C.

VI. Summary

The following significant results were obtained from this work:

- The laboratory carbothermic synthesis of uranium-plutonium mixed nitride $(U_{0.80}Pu_{0.20})N$ from individual oxides of uranium and plutonium was found to be practical.
- A single phase nitride product was consistently obtained from the carbothermic process.
- The use of a reaction sequence involving the nitridation of the carbonitride phase and the reduction of excess carbon with hydrogen was successful in controlling the carbon content of the product.
- The composition of the nitride product in successive runs showed little variation.
- The entire synthesis process was successfully carried out in an all refractory metal particle-bed reactor.
- The rate of the carbothermic reaction between 1430°C and 1625°C increases with temperature in an Arrhenius manner.

TABLE II

Kinetic Measurements for the Carbothermic Reduction of the Dioxides of
Uranium and Plutonium in Flowing Nitrogen

Sample Number	Sample	Nitrogen Flow Rate (cc/min/gm)	Sample Particle Size (Mesh)	Sample Weight (g)	Initial Carbon Content (wt. %)	Reaction Temp. (°C)	1st Order Rate Constant	-lnk
L-1	4:1 UO ₂ , PuC ₂ in tungsten boat	97	+ 100, - 60	10.0	9.3	1430	0.0061	5.12
L-2	"	98	+ 100, - 60	10.0	9.3	1625	0.030	3.51
L-3	"	97	+ 100, - 60	10.0	9.3	1500	0.011	4.51
L-4	"	96	+ 100, - 60	10.0	9.3	1518	0.011	4.51
L-5	"	96	+ 100, - 60	10.0	9.3	1455	0.0065	5.04
UP-3	4:1 UO ₂ , PuO ₂ Production	40	+ 60, - 28	50.0	9.3	1600	0.019	3.96
UP-4	Runs in Reactor	40	+ 60, - 28	50.0	8.7	1600	0.014	4.27
UP-6	"	40	+ 60, - 28	50.0	8.7	1600	0.015	4.20
UP-7	"	40	+ 60, - 28	50.0	8.7	1600	0.013	4.51
UP-8	"	60	+ 60, - 28	50.0	8.7	1600	0.019	3.96
UP-9	"	70	+ 60, - 28	100.0	8.7	1600	0.036	3.32

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PARTICLE BED REACTOR SYSTEM FOR CARBOTHERMIC SYNTHESIS OF URANIUM - PLUTONIUM NITRIDES

KINETICS OF THE CARBOTHERMIC SYNTHESIS OF 80% URANIUM-20%
PLUTONIUM MONONITRIDE