NASA CR-134498
ORNL-TM-4496

CONTINUATION OF DEVELOPMENT OF NITRIDES FOR SPACE NUCLEAR REACTORS

R. A. Potter
J. L. Scott

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

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by

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NASA Lewis Research Center
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Robert R. Metroka, Project Manager

CONTENTS

CONTINUATION OF DEVELOPMENT OF NITRIDES FOR SPACE NUCLEAR REACTORS

R. A. Potter[1] and J. L. Scott

ABSTRACT

Alloy nitrides of (U,Zr), (U,Ce), and (U,Y) were prepared and exposed to vacuum at temperatures to 1700°C (1973 K) and compared with pure UN. Weight loss data and physical observations showed that the alloy samples were more stable than UN. For example, in weight loss, (U,Zr)N was 3 times as stable as UN at 1600°C (1873 K) for 100 hr at 2×10^{-6} torr (2.66×10^{-4} N/m^2).

INTRODUCTION

Uranium mononitride (UN) is an attractive nuclear fuel because of its high density, high melting point, and high thermal conductivity. In addition, it has shown[2] excellent irradiation stability up to 2 at. % burnup at temperatures up to 1773 K (1500°C). A possible hindrance to the use of UN at higher temperatures is its dissociation into uranium liquid and nitrogen gas under reduced pressures.[3]

The main purpose of the present work was to investigate the ability of additives to UN to lower the dissociation constant or the rate of decomposition at 1600 to 1700°C (1873 to 1973 K). The specific additives selected for this cursory test were zirconium, yttrium, and cerium nitrides because of their solid solubilities in UN and their greater stabilities than UN.

A second objective was to produce a variety of sintered UN specimens of specific chemical purity, size, density, and ^{235}U enrichment for delivery to the Lewis Research Center of the National Aeronautics and Space Administration (NASA-Lewis). This is the final report under Interagency Agreement AEC 40-342-72, NASA Order C-16968C.

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[1]Present address, Babcock & Wilcox, Lynchburg, Va.

[2]V. J. Tennery, T. N. Washburn, and J. L. Scott, "Fabrication and Irradiation Behavior of Uranium Mononitride," pp. 587–600 in *Ceramics in Severe Environments, Materials Science Research*, Vol. 5, ed. by W. W. Kriegel and H. Palmour III, Plenum Press, New York, 1971.

[3]H. Inouye and J. M. Leitnaker, "Equilibrium Nitrogen Pressure and Thermodynamic Properties of UN," *J. Amer. Ceram. Soc.* 51(1): 6–9 (1968).

PREPARATION OF NITRIDE SAMPLES FOR THERMAL STABILITY TESTS

Attempts to prepare alloys of 10 mole % Zr, Y, and Ce in uranium were conducted in 250-g batches by arc-melting procedures designed to yield homogeneous mixtures. High-purity melt stock of each metal was cleaned by acid pickling or electrolytic etching, batched with twice its weight of cleaned, depleted uranium metal, and arc-melted under argon at least four times with stirring to produce a master mix. This master mix was then remelted with the balance of the uranium at least six times, again with stirring. In each case, melting was accomplished without difficulty.

The alloy buttons were removed from the arc furnace, cleaned with dilute nitric acid, and immediately transferred into an argon glove box for loading into the synthesis retort. Nitride powders were prepared from the alloys by the standard hydride-dehydride-nitride procedures developed previously for pure uranium nitride.[4] Synthesis proceeded normally, and the resulting nitride powders were essentially indistinguishable from pure UN. The powder batches were stored in sealed jars in an argon glove box. Specimens of each alloy composition and also of pure UN were prepared by isostatic pressing without binders at 60,000 psi (4.1×10^8 N/m^2) and sintering at 2300°C (2573 K) by procedures described previously.[4]

Complete characterization of the sintered pieces was not undertaken because of the limited scope of this investigation, but a few significant results were obtained and are shown in Table 1. The (U,Zr)N samples were

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[4]V. J. Tennery, T. G. Godfrey, and R. A. Potter, *Synthesis, Characterization, and Fabrication of UN*, NASA-CR-72764; ORNL-4608 (December 1970).

Table 1. Characterization of Nitride Specimens for Thermal Stability Tests

	UN	(U,Zr)N	(U,Y)N	(U,Ce)N
Chemical Analysis				
U, wt %	94.50	90.51	94.63	[a]
N, wt %	5.45	5.51	5.45	[a]
O, ppm	320	204	[a]	[a]
C, ppm	400	361	[a]	[a]
Zr, Y, or Ce, wt %		3.40	0.22	3.05
Mole %, Second Metal		8.93	0.62	5.41
X-Ray Lattice Parameter	4.889	4.856	4.889	4.893
Mole %, Second Metal[b]		11	[c]	4
Density, g/cm^3	13.38	13.16	13.30	[a]

[a]Not determined.

[b]Vegard's law assumed to apply.

[c]Lattice parameter of YN too close to UN to allow estimate.

the first made and hence were the most thoroughly analyzed. The composition is acceptably close to the desired 10 mole %. The yttrium sample is puzzling in its very low yttrium content since all steps in its preparation seemed to progress normally. Similarly, the cerium sample contains only about half the intended cerium. We assume that yttrium and cerium were lost by vaporization during melting. Insufficient time prevented investigation of these anomalies.

PRELIMINARY THERMAL STABILITY TESTS

Tests on (U,Zr)N at 1600 and 1700°C

As-sintered pieces of UN and (U,Zr)N approximately 1/4 in. diam × 1 in. long (0.635 × 2.54 cm) were placed on tungsten plates in a cold-wall vacuum furnace with a tungsten-mesh element and a manually controlled power supply. The samples were heated at 1600°C (1873 K) under vacuum of 1×10^{-5} torr (1.3×10^{-3} N/m^2) for a total of 8 hr, with intermediate weighings after 1 and 4 hr. The test temperature was then raised to 1700°C (1973 K) at the same pressure for an additional 8 hr with similar intermediate weighings. It should be noted that these temperatures were determined periodically by use of an optical pyrometer and are subject to a ±10°C precision.

The results of the 1600 and 1700°C tests (Fig. 1) show that at 1600°C (1873 K) the rate of weight loss of the (U,Zr)N sample was about half that of UN, but at 1700°C (1973 K) it was about three-fourths that of UN. The slight increase in rate of weight loss observed between 12 and 16 hr is judged to be a temperature effect since examination of the furnace log book revealed that the power level was slightly higher for the final hours of the test. We estimate that the power increase could have led to at least a 30°C temperature rise during this time.

Microstructures of the UN and (U,Zr)N samples as sintered and after test are shown in Fig. 2. Minute traces of uranium metal may be seen in the UN sample (b) after 8 hr at 1600°C, while its companion (U,Zr)N is free of any metal. After the additional 8 hr at 1700°C, however, both samples (c) contain free uranium metal. For the (U,Zr)N sample, the metal is located for the most part only near the surface of the sample, whereas the pure UN sample has free metal distributed throughout. It appears that the UN sample contains several times as much free metal as does the (U,Zr)N sample.

Tests on UN, (U,Ce)N, (U,Y)N, and (U,Zr)N at 1700°C

As-sintered pieces of UN and the three alloy nitrides were exposed for a total of 25 hr at about 1700°C (1973 K) to a vacuum of about 1×10^{-5} torr (1.3×10^{-3} N/m^2). The results for the three alloy nitrides

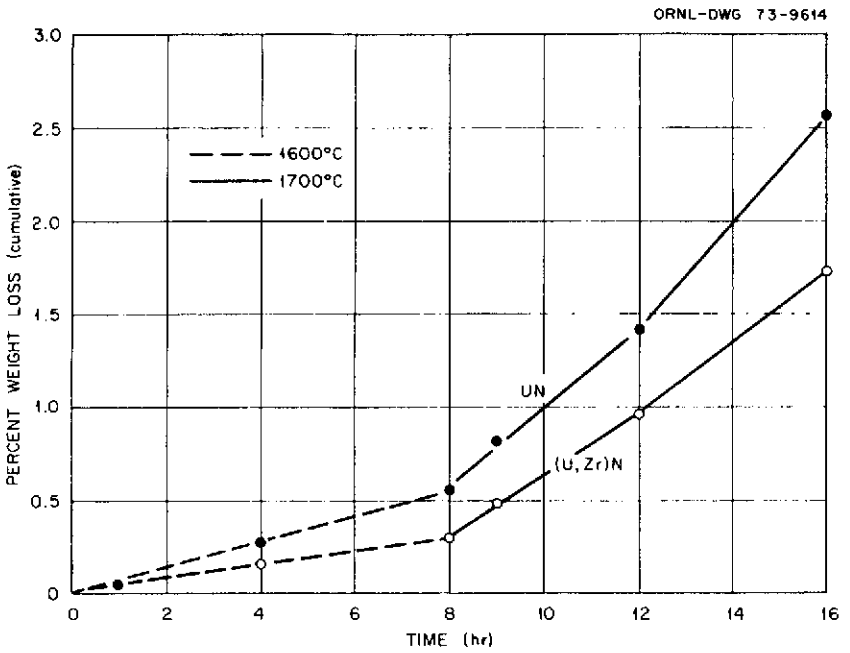

Fig. 1. Effect of Time and Temperature on the Weight Loss of Pure UN and $U_{0.9}Zr_{0.1}N$ in a Vacuum of 1×10^{-5} torr (1.3×10^{-3} N/m^2).

are shown in Fig. 3. It should be noted that the three alloy nitride samples were tested separately, and that only for the (U,Ce)N case was pure UN tested simultaneously. Thus, quantitative comparisons of these tests are not straightforward, but the differences are sufficiently gross that the trends are quite evident. The pure UN sample dissociated to the extent that it stuck to the tungsten setter plate after only 1 hr. Therefore weight data were not obtained for UN for plotting on Fig. 3. The resultant microstructure of the UN (Fig. 4) clearly shows the gross free metal. The (U,Ce)N sample had a large weight loss, but unaccountably did not stick to the tungsten, although its microstructure after 17.5 hr (Fig. 5) shows more free metal than the UN. The (U,Y)N sample was stuck to the tungsten after 19 hr, even though it had a weight loss half that of the (U,Ce)N sample. Its microstructure, Fig. 6, shows large amounts of free metal throughout. The (U,Zr)N piece exhibited the smallest weight loss, but its microstructure, Fig. 7, also shows a significant amount of free metal.

Comparison of these results with the previously described results on UN and (U,Zr)N at 1600 and 1700°C as noted earlier is not straightforward. The quantity of free metal in the 25-hr 1700°C tests is much greater than that in those for 8 hr at 1600°C plus 8 hr at 1700°C, while the weight loss in 25 hr at 1700°C is much less. It would appear that in the two-temperature tests the vaporization was almost congruent, but in the 25-hr 1700°C tests it was very incongruent. An explanation for this behavior is that possible oxygen contamination of the furnace atmosphere in the 8-hr tests could enhance the vaporization of the free metal via a UO species. This cannot be substantiated but would account for the noted observations.

The results on the (U,Ce)N and (U,Y)N samples indicate that their decomposition behavior was superior to that of the pure UN if judged

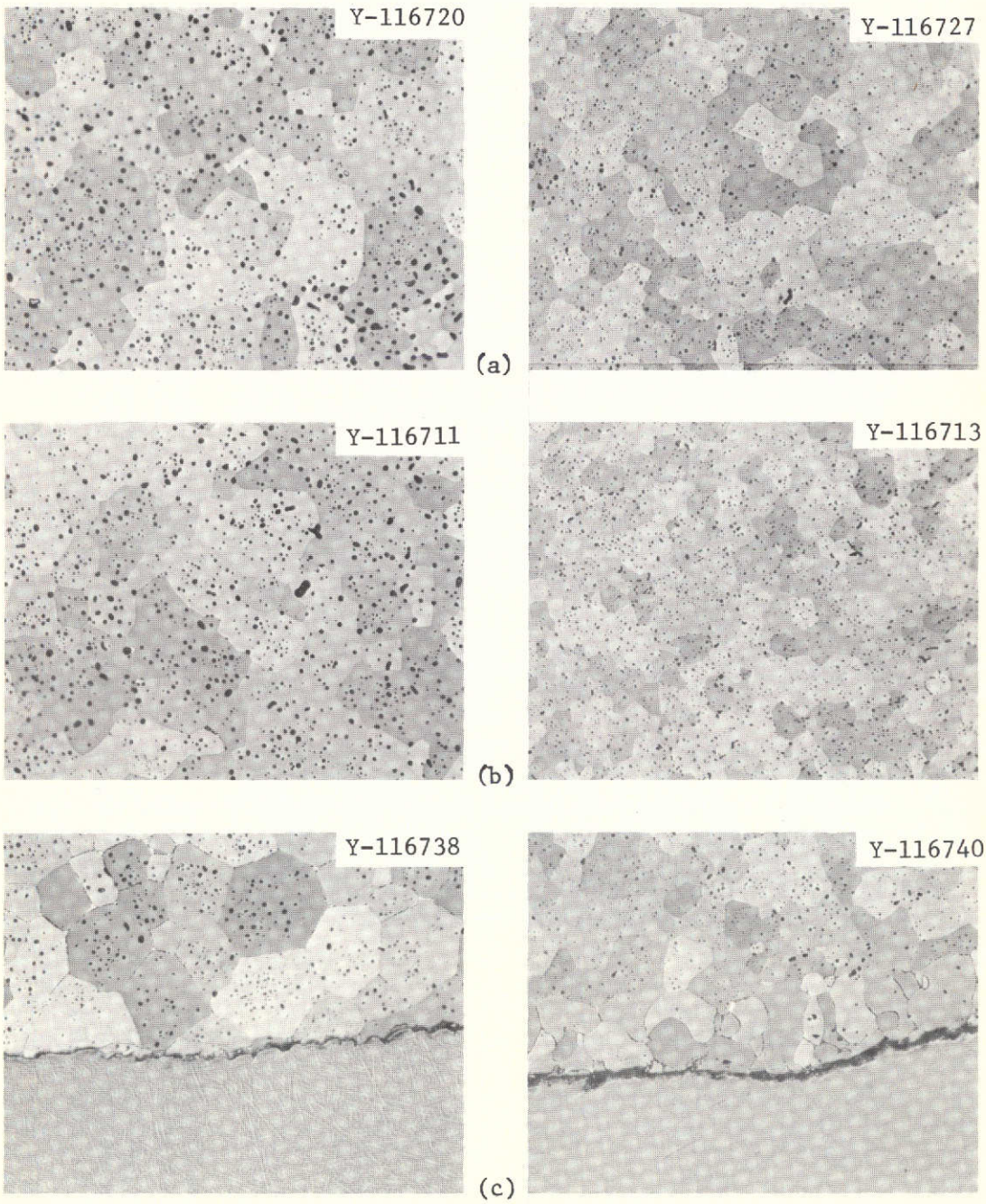

Fig. 2. Microstructures of (left) Pure UN Samples and (right) $U_{0.9}Zr_{0.1}N$. Lactic, nitric, and hydrofluoric acid etchant. 100×. (a) As sintered. (b) After 8 hr at 1600°C (1873 K) under vacuum of 1×10^{-5} torr (1.3×10^{-3} N/m^2). (c) After 8 hr at 1600°C and 8 hr at 1700°C (1973 K) under vacuum.

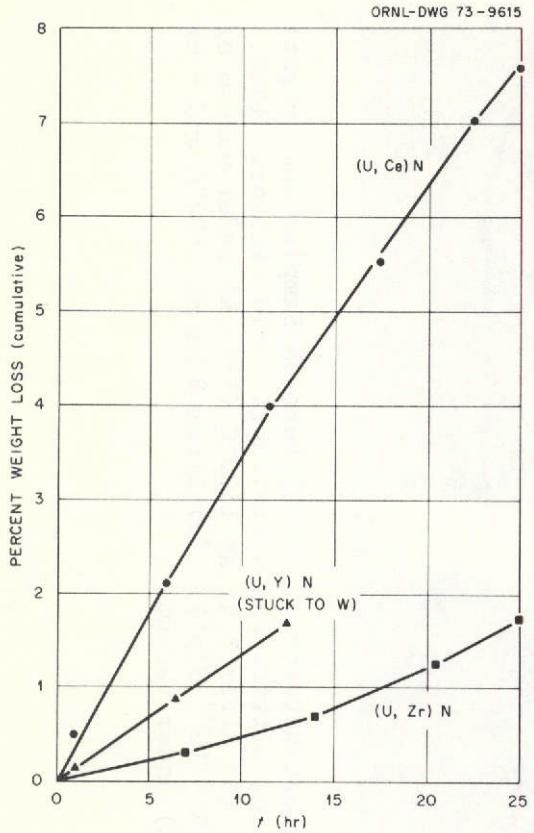

Fig. 3. Weight Loss of Nitride Alloy Specimens with Time at 1700°C (1973 K). A pure UN companion sample to the (U,Ce)N was stuck to the tungsten setter after 1 hr and could not be weighed.

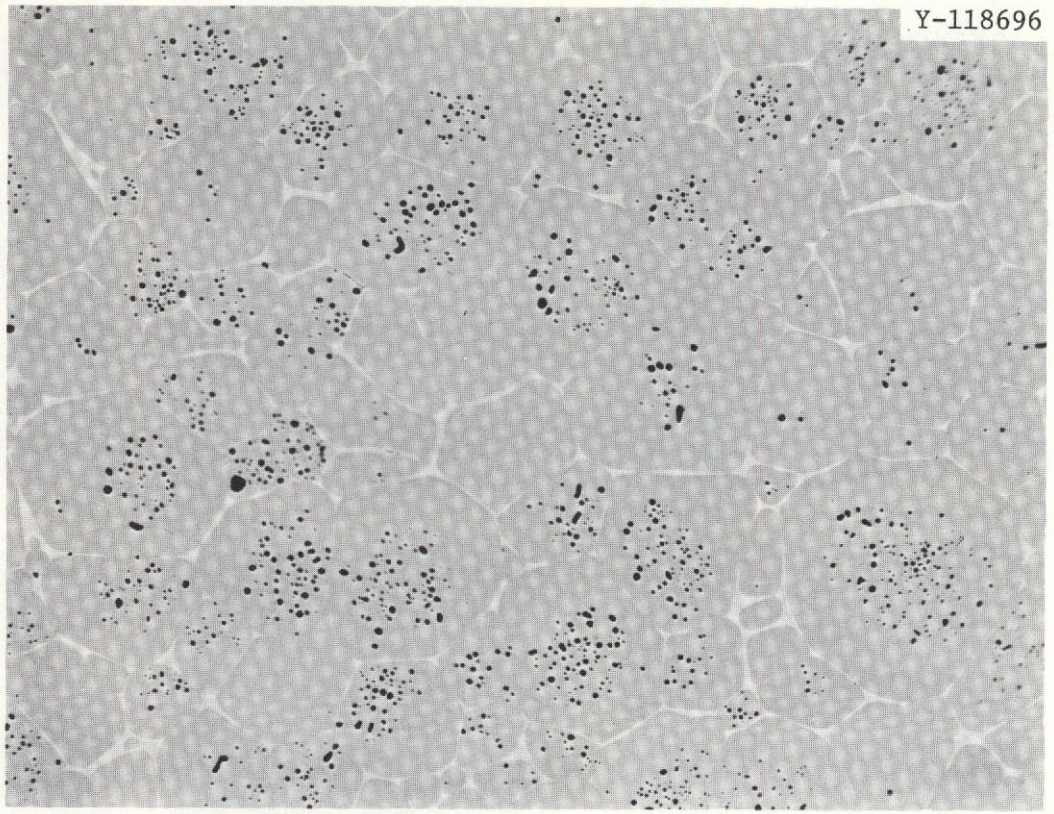

Fig. 4. Microstructure of Pure UN Sample After 25 hr at 1700°C (1973 K) Under Vacuum of 1×10^{-5} torr ($1.3 \times 10^{-3} N/m^2$), Showing Gross Free Metal (White Phase) Surrounding UN Grains. As polished. 100×.

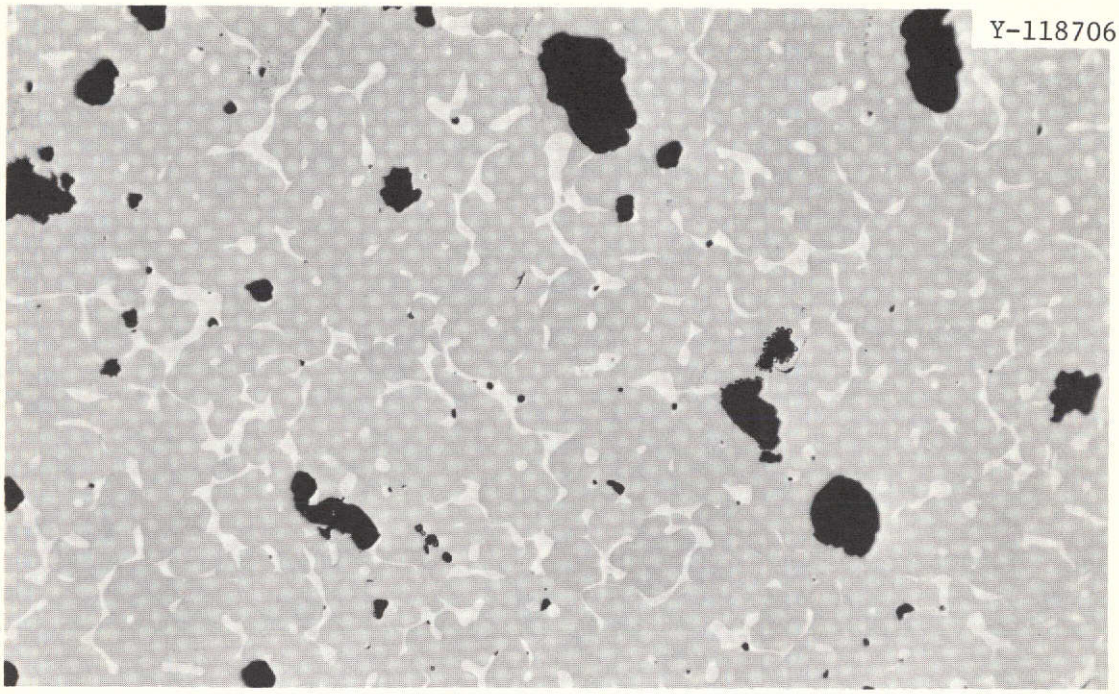

Fig. 5. Microstructure of (U,Ce)N Sample After 17.5 hr at 1700°C (1973 K) Under Vacuum of 1×10^{-5} torr (1.3×10^{-3} N/m^2), Showing Gross Free Metal (White Phase) Surrounding Nitride Grains. As polished. 100×.

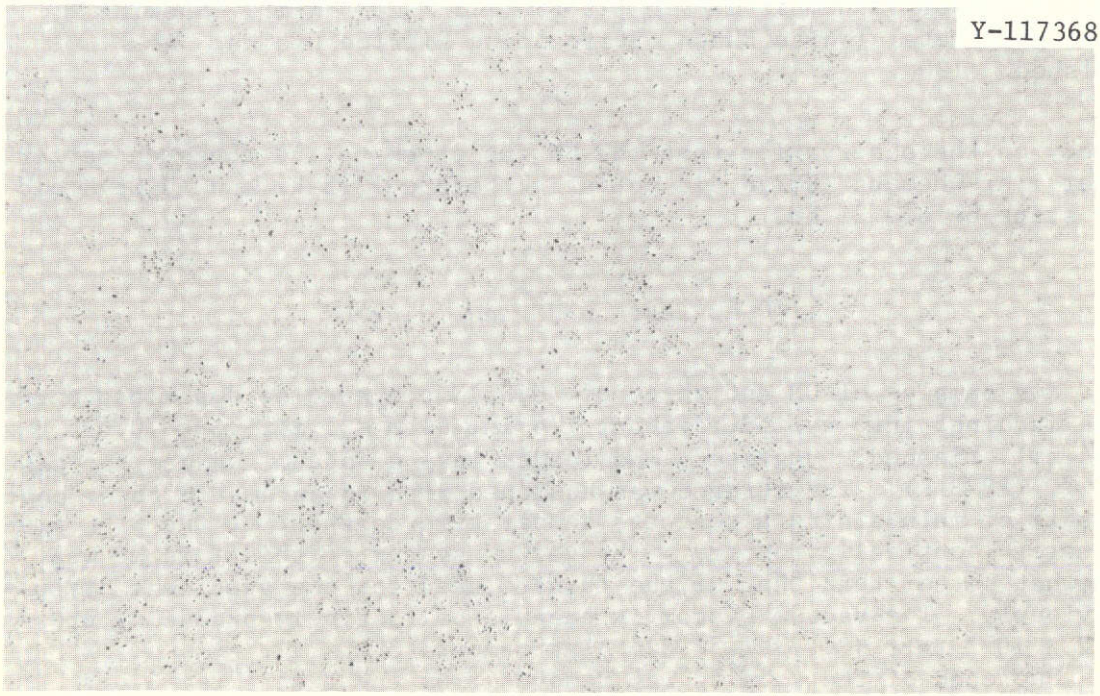

Fig. 6. Microstructure of (U,Y)N Sample After 25 hr at 1700°C (1973 K) Under Vacuum of 1×10^{-5} torr (1.3×10^{-3} N/m^2), Showing Gross Free Metal (White Phase) Surrounding Nitride Grains. As polished. 50×.

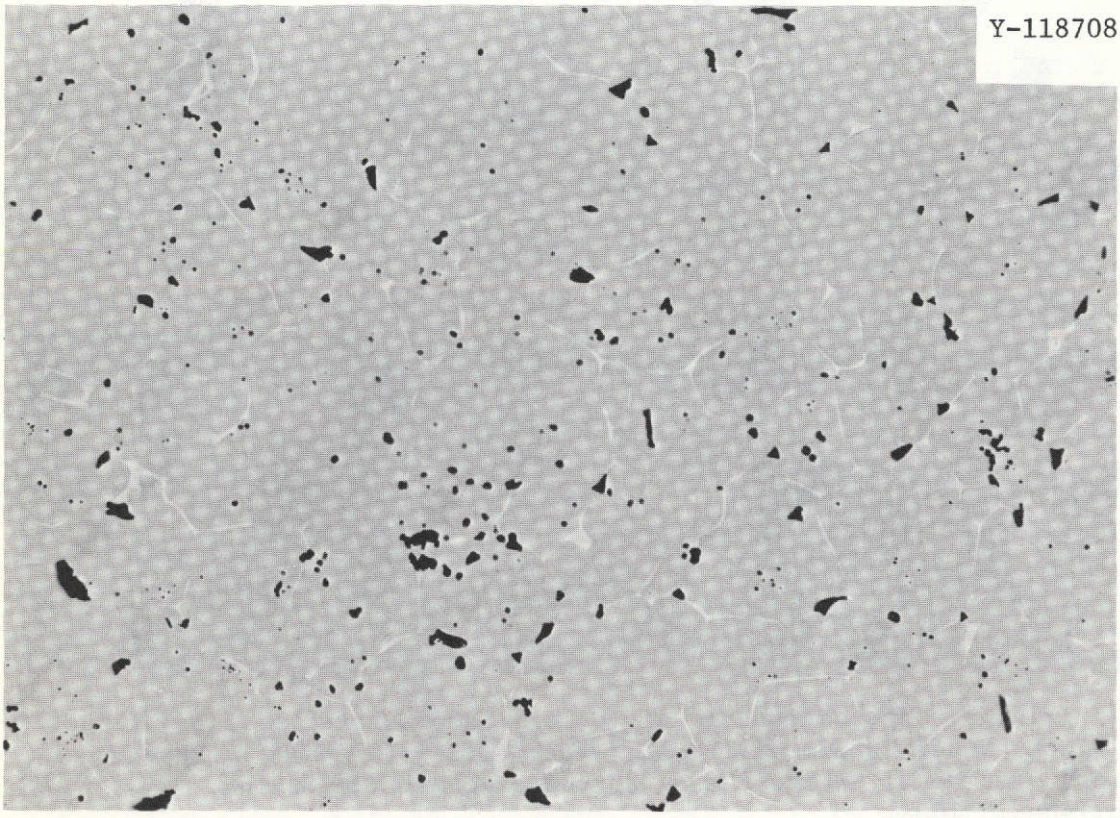

Fig. 7. Microstructure of (U,Zr)N Sample After 25 hr at 1700°C (1973 K) Under Vacuum of 1×10^{-5} torr (1.3×10^{-3} N/m^2), Showing Gross Free Metal (White Phase) Surrounding Nitride Grains. As polished. 100×.

solely on the observation that the UN was stuck to the tungsten setter after 1 hr whereas (U,Y)N did not stick before 12.5 hr and (U,Ce)N did not stick before 25 hr.

100-hr Test on UN and (U,Zr)N

Two samples of UN and three of (U,Zr)N prepared as described earlier were machined into cylinders about 1/4 in. diam × 1 in. long (0.635 × 2.54 cm), cleaned, outgassed, and loaded into a vacuum furnace for tests at 1600°C (1873 K). The furnace was equipped with an automatic power controller capable of maintaining a selected temperature constant to the ±5°C precision of careful optical pyrometry. The vacuum system of this furnace was somewhat better than that of the furnace used for the specimens discussed previously. The vacuum system is capable of routinely producing pressures of 2×10^{-6} torr (2.7×10^{-4} N/m^2) at temperature.

One each of the samples was removed from the test after 8 hr. Remaining samples were heated at 1600°C for a total of 100 hr. The

pre- and post-test dimensions and weights of these samples are shown in Table 2. All samples decreased in dimensions and weight, and calculated bulk densities increased by about 2% in 100 hr. The weight loss of the (U,Zr)N samples was about one-third that of the pure UN, indicating a significant increase in thermal stability. The microstructures of these samples after 100 hr, shown in Fig. 8, reveal that the (U,Zr)N contained much less free metal than did the pure UN, and the quantity correlates with the observed weight losses and density increases. Testing of other compositions for 100 hr was precluded by a lack of funds.

Table 2. Weight and Dimensional Data on UN and $U_{0.9}Zr_{0.1}N$ Tested at 1600°C (1873 K) Under Vacuum of 2×10^{-6} Torr (2.7×10^{-4} N/m^2)

	UN Samples		$U_{0.9}Zr_{0.1}N$ Samples		
	1UN	2UN	1UZN	2UZN	3UZN
Weight, g					
before test	14.7049	4.1393	13.5004	14.9065	12.8363
after 8 hr	14.6948	4.1356	13.4972	14.9032	12.8333
after 100 hr	14.5968		13.4671	14.8717	
Weight loss,					
after 8 hr, %	0.0687	0.0894	0.0237	0.0221	0.0234
after 8 hr, %/hr	0.00858	0.01117	0.00296	0.00277	0.00292
after 100 hr, %	0.7351		0.2466	0.2334	
after 100 hr, %/hr	0.00735		0.00247	0.00233	
Diameter, in.					
before test	0.2497	0.3101	0.2755	0.2755	0.2755
after 8 hr	0.2497	0.3098	0.2754	0.2753	0.2755
after 100 hr	0.2472		0.2737	0.2736	
Length, in.					
before test	1.3870	0.2472	1.0670	1.1750	0.9755
after 8 hr		0.2470			0.9751
after 100 hr	1.377		1.061	1.068	
Density,[a] g/cm^3					
before test	13.212	13.530	12.952	12.987	13.470
after 8 hr		13.55			13.473
after 100 hr	13.478		13.165	13.216	
Density increase, %					
after 8 hr		0.186			0.020
after 100 hr	2.02		1.64	1.76	

[a]Calculated from geometric volume and weight.

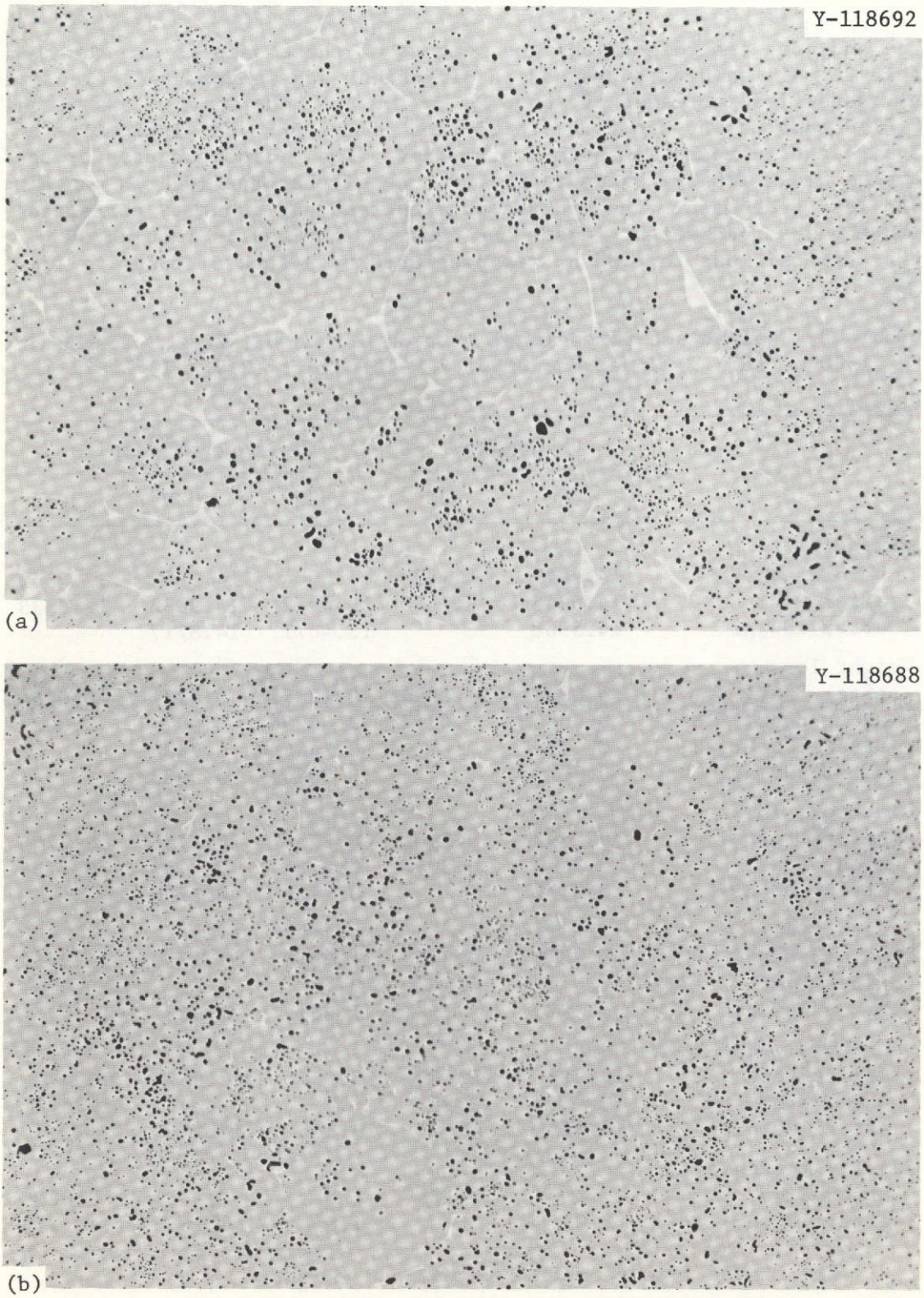

Fig. 8. Microstructure of Samples After 100 hr at 1600°C (1873 K) Under Vacuum of 2×10^{-6} torr (2.76×10^{-4} N/m^2). As polished. 100×.
(a) Pure UN showing extensive free uranium at grain boundaries.
(b) $U_{0.9}Zr_{0.1}N$ showing slight free metal.

PRODUCTION OF UN FUEL FORMS

During the course of this work, UN pellet test specimens, with the chemical and physical parameters shown in Table 3, and representing contract line items, were delivered to NASA-Lewis. The samples were cold formed by isostatically pressing as-synthesized nitride powders at 60,000 psi (4.1×10^8 N/m^2) according to procedures established jointly by NASA-Lewis and ORNL during previous investigations.[5] The specimens

Table 3. UN Test Specimens Delivered to NASA-Lewis Research Center

Line Item[a]	Number of Pieces	Bulk Density (% of theoretical)	Oxygen Content (ppm)	Nominal Dimensions, in.			^{235}U Enrichment (%)
				OD	ID	Length	
1	89	95.4	339	0.310	0.099	0.250	Depleted
4	1	94.3	237	0.622	0.299	1.499	5.03
5	2	92.9	120	0.622	0.299	0.750	5.03

[a]Line items 2 and 3 were cancelled at direction of Project Manager.

were sintered at 2350°C (2623 K) and 760 torr (1.0×10^5 N/m^2) nitrogen for 3 hr. The initial heatup was done in vacuum to 1450°C (1723 K), the furnace backfilled with nitrogen at a pressure of 760 torr, and the temperature increased to 2350°C (2623 K). After the 3-hr sintering period, the temperature was lowered to 1450°C (1723 K), and the furnace was evacuated and allowed to cool to room temperature.

The sintered specimens were machined to tolerances as follows: outer diameter, ±0.0005 in. (13 μm); inner diameter, ±0.001 in. (25 μm); length, ±0.002 in. (51 μm); and concentricity, 0.004 in. (0.10 mm). According to procedures and techniques established during previous investigations,[5] the specimens were centerless ground and end faced. The axial holes in the bushings were made by the electrodischarge machining (EDM) method. On completion of machining, the pieces were ultrasonically cleaned in ethanol and then heat treated in vacuum for 1 hr at 1400°C (1673 K).

The microstructure of a line item 1 piece is shown in Fig. 9 to be free of second-phase material and is representative of all UN samples made in this laboratory.

In addition to the specimens described in Table 3, considerable progress was made on two line items that were cancelled by the Project Manager. Pressed and sintered rods of UN made with 52%-enriched ^{235}U were ready to be machined into 18 pieces similar in dimensions to line

[5]V. J. Tennery, T. G. Godfrey, and R. A. Potter, *Synthesis, Characterization, and Fabrication of UN*, NASA-CR-72764; ORNL-4608 (December 1970).

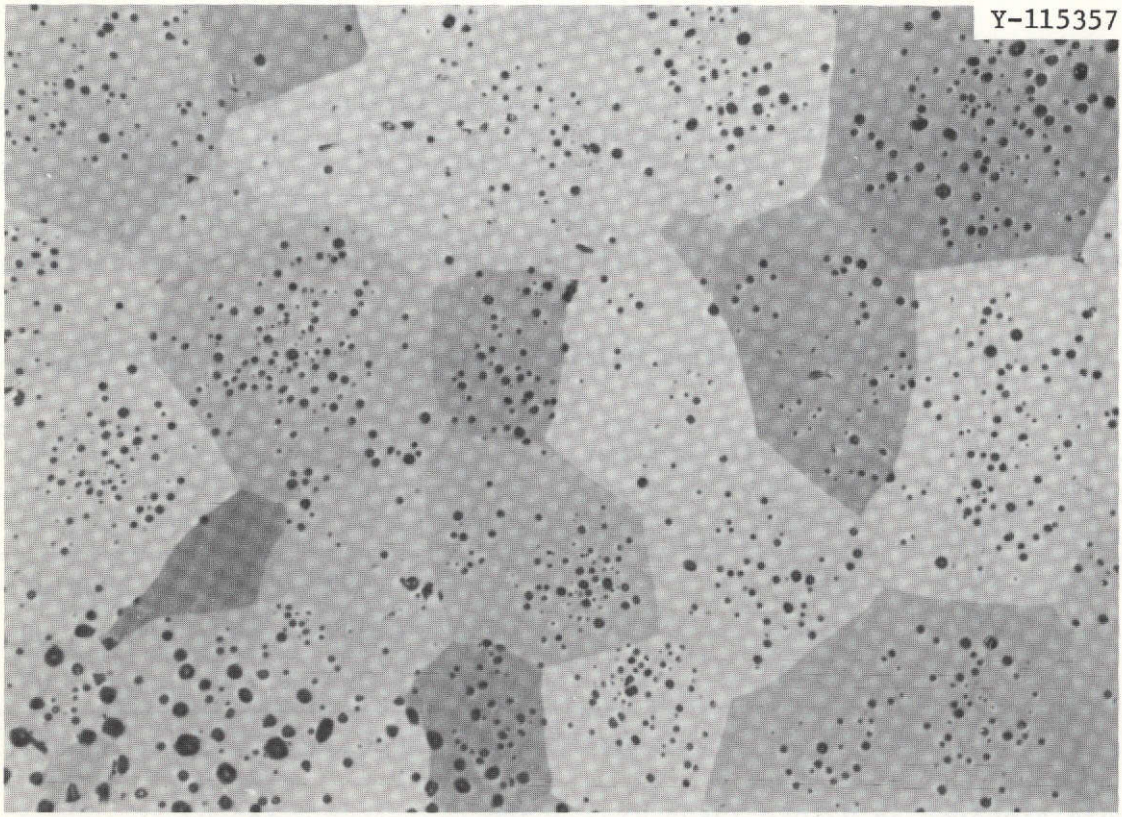

Fig. 9. Microstructure of Fuel Form of Line Item 1 Uranium Mononitride. Etched with lactic, nitric, and hydrofluoric acids. 500×.

item 1. Also, a 1-kg batch of depleted UN had been synthesized to make a set of large bushings similar to line item 4.

CONCLUSIONS AND OBSERVATIONS REGARDING THERMAL STABILITY

1. Compacts of alloy nitrides were prepared from arc-melted alloys of U-Zr, U-Ce, and U-Y by hydride-nitride synthesis, isostatic pressing, and sintering in nitrogen at 2300°C (2573 K). The (U,Zr)N sintered material was of high quality, while the (U,Ce)N and (U,Y)N were lower in alloy element content than intended.
2. Thermal stability tests showed that $U_{0.9}Zr_{0.1}N$ is two to three times more stable than UN in terms of weight loss and amount of free uranium formed up to 1600°C (1873 K).
3. Insufficient work was done to allow one to draw conclusions about the stability of (U,Y)N and (U,Ce)N relative to UN.

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