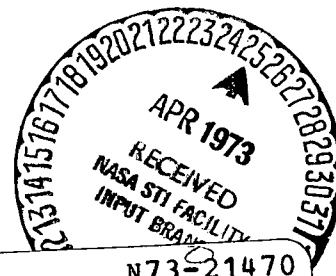NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Memorandum 33-602

Uranium Nitride Behavior at Thermionic Temperatures

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JET PROPULSION LABORATORY

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

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16. Abstract

The feasibility of using uranium nitride for in-core thermionic applications was evaluated in electrically heated thermal gradient tests and in flat plate thermionic converters. These tests indicated that grain boundary penetration of UN into both tungsten and rhenium will occur under thermal gradient conditions. In the case of the tungsten thermionic converter, this led to grain boundary rupture of the emitter and almost total loss of electrical output from the converter. It appears that uranium nitride is unsuitable for thermionic applications at the 2000 K temperatures used in these tests.

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PREFACE

The work described in this report was performed by the Propulsion
Division of the Jet Propulsion Laboratory.

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ABSTRACT

The feasibility of using uranium nitride for in-core thermionic applications was evaluated in electrically heated thermal gradient tests and in flat plate thermionic converters. These tests indicated that grain boundary penetration of UN into both tungsten and rhenium will occur under thermal gradient conditions. In the case of the tungsten thermionic converter, this led to grain boundary rupture of the emitter and almost total loss of electrical output from the converter. It appears that uranium nitride is unsuitable for thermionic applications at the 2000 K temperatures used in these tests.

I. INTRODUCTION

Uranium nitride has a high uranium density and a high-temperature melting point which make it appear attractive for in-core nuclear thermionic applications. To evaluate uranium nitride behavior under thermionic operating conditions, three tests were run using out-of-pile electrical heating: (1) gross compatibility of uranium nitride and tungsten in contact at thermionic emitter temperatures with a thermal gradient, (2) a thermionic converter with uranium nitride encapsulated in the tungsten emitter, and (3) a thermionic converter with uranium nitride encapsulated in a rhenium emitter.

II. THERMAL GRADIENT TEST WITH TUNGSTEN

The capsule used to determine gross compatibility at thermionic operating conditions of uranium nitride and tungsten is shown in Fig. 1. The key features of the experiment are (1) a tungsten-clad uranium nitride sample, (2) a thermal gradient in the fuel capsule, (3) a vent hole orifice, and (4) an additional sealed chamber containing hafnium to simulate the materials in an actual thermionic fuel element which could act as a sink for the nitrogen.

The uranium nitride used in the experiment was made by arc-melting uranium as a consumable electrode under 20 atmospheres of nitrogen. The resulting casting was heat-treated at 1450°C in a vacuum of approximately 0.1 N/m^2 (10^{-3} torr) to decompose any higher nitrides formed during arc-melting. The uranium nitride was then canned in tantalum and hot-isostatically-pressed to densify the material.

Tungsten used for the test capsule was made from fluoride-vapor-deposited tubing with high-purity powder metallurgy tungsten (GE-13) for the

end caps and orifice plate. The hafnium used was high-purity arc-cast material.

The capsule assembly was fabricated by electron beam welding at approximately $10^{-3}N/m^2$ (10^{-5} torr). Testing was done in a vac-ion pumped furnace at approximately $10^{-5}N/m^2$ (10^{-7} torr). The upper end cap was maintained at 1800° C. The thermal gradient was produced by proper positioning of the capsule within the hot zone and using a heavy capsule support stand as a heat sink. This configuration resulted in a temperature of 1500° C at the lower end cap. Total time at temperature was 1000 hours, after which the capsule was sectioned and examined metallographically.

Metallographic examination of the test capsule revealed a very good bond between the uranium nitride (UN) and the tungsten at the point of contact. The uranium nitride after test is shown in Fig. 2. Metallographic examination did not detect any free uranium. Previous work (Ref. 1) detected free uranium, particularly in the grain boundaries of $UN_{0.99}$. The composition of the nitride after test appears very close to stoichiometric. No chemical reaction was detected in either the UN or the tungsten. Microhardness measurements of the tungsten at the bond area indicated the Knoop hardness to be 250 ±20. The scatter in hardness measurements appeared to result from various grain orientations of the tungsten rather than a function of depth from the bonded surface. This hardness is lower than typically quoted for tungsten (Ref. 2), indicating the material to be relatively high purity and fully recrystallized, as shown in Fig. 3.

Redistribution of the uranium nitride took place along the counter-bored hole on the orifice plate (Fig. 3). This was the only area within the capsule where redistribution was observed. In addition, diffusion of uranium nitride into the tungsten occurred (Fig. 4). A continuous network of uranium nitride is visible in the grain boundaries of the tungsten as well as uranium nitride particles within the tungsten grains. However, no evidence of free uranium was observed in these uranium nitride particles.

III. THERMIONIC CONVERTER TEST WITH TUNGSTEN EMITTER

A schematic of the converter is shown in Fig. 5. The converter is a flat plate design with electrode areas of 1.81 cm^2 and interelectrode spacing

of 0.025 cm. The emitter (Fig. 6) was made from arc-cast tungsten and fueled with just one uranium nitride pellet in the center hole of the available seven holes. The remaining six holes were left empty. The uranium nitride fuel was made by the same process as that used in the thermal gradient test. The collector was niobium.

The converter was characterized and subsequently life-tested at an emitter temperature of 1900 K (Ref. 3). The power output of the converter increased slowly from 2.2 to 3.9 W/cm^2 at 4300 h as shown in Fig. 7, possibly because of the self-cleaning of the emitter. At 4735 h the output power suddenly degraded to 2.1 W/cm^2 within 2.5 h (Fig. 8). Reoptimization of collector and cesium temperature for maximum power required increasing the cesium temperature T_R 90 K to 703 K and increasing the collector temperature T_C 89 K to 1027 K. The new value of power density was 3.68 W/cm^2 at 4739 h, but the output power density decreased, at a slower rate, to 0.66 W/cm^2 in 16 h. The output power density was again restored to 3.3 W/cm^2 at 4756 h by mainly increasing T_C to 1079 K; T_R was increased only 14 K to a new value of 717 K. The output power density degraded thereafter to 0.39 W/cm^2 within 16 h of reoptimization. The life test was terminated at 4775 h since the power output density could not be restored.

The converter was disassembled for examination and determination of the causes of thermionic performance degradation. The emitter surface is shown in Fig. 9 and the collector surface in Fig. 10. The uranium nitride pellet location is obvious by the yielding of the tungsten emitting surface over the fuel pellet, particularly at grain boundaries. The collector surface opposite the fuel pellet was darkened (Fig. 10).

The emitter was sectioned through the fuel pellet. This section is shown in Fig. 11. This photomicrograph indicates some evidence of reaction between the fuel and tungsten. The more obvious effect was the grain boundary penetration of the fuel into the tungsten as shown in the high magnification view in Fig. 12.

A metallographic section of the collector surface is shown in Fig. 13. The darkened area on the collector surface (Fig. 10) appears to be a scattered surface reaction layer which produced a second phase. Microhardness data indicated surface hardening of collector, 143 KHN (Knoop hardness number) at a depth of 0.02 mm from the electrode surface,

decreasing to 120 KHN at 0.2 mm or greater from the electrode surface. The hardnesses are greater than those typically observed for niobium, about 100 KHN. The tungsten emitter also appeared hardened. Readings varied between 550 and 650 KHN near the uranium nitride fuel pellet as compared to approximately 475 KHN in other areas of the emitter.

Ion scattering analyses of both emitter and collector surfaces were run. This technique provides the composition of the surface to depths of several monolayers for all elements heavier than helium which are present in amounts greater than approximately 1 atom % (the limit of detection). The composition as a function of depth can also be obtained, and this data for the emitter is shown in Fig. 14. Other elements detected on the surface of the emitter in amounts of several percent were as follows:

Element	Possible source
Aluminum	Al_2O_3 seal
Calcium or potassium	Cesium impurity
Copper	Seal braze material

Nitrogen, uranium, and niobium were detected on the emitter surface but at levels just above the limits of detection (~1 atom %).

Analyses of the collector (Fig. 15) indicated significant transfer of tungsten from the emitter to the collector. These analyses indicated the formation of a layer greater than 150 monolayers thick produced by the transfer of tungsten, the trapping of cesium, and the outward diffusion of niobium from the collector base material. The niobium may be present in the form of oxide since the oxygen concentration is sufficient to produce NbO.

The collector surface also displayed the presence of several percent of aluminum, calcium, or potassium and copper, as did the emitter. In addition, several percent of sodium was detected, presumably introduced as an impurity in the cesium and alumina seal materials. Uranium and nitrogen were also detected at the 1 atom % level as they were in the emitter.

The presence of uranium and nitrogen on both collector and emitter substantiates the metallographic observations indicating transport of the fuel through the tungsten. Since the analyses samples were not taken from

the UN fuel pellet area, large concentrations of uranium and nitrogen would not be expected.

It can be postulated that the low initial performance of the converter was due to the low work function of the emitter. As the oxygen/cesium/tungsten layer built up on the electrode surfaces, performance increased until grain boundary rupture of the emitter occurred, producing the reaction layers on the collector shown in Figs. 10 and 13 and the associated rapid performance degradation.

IV. THERMIONIC CONVERTER TEST WITH RHENIUM EMITTER

A second converter with a uranium-nitride-fueled rhenium emitter of the same design as the first converter is currently undergoing a life test (Ref. 4). This converter displayed a degradation of output after 1000 h of testing (Fig. 16). The life test was interrupted occasionally to make diagnostic measurements, including the work function measurements, whenever a noticeable change occurred in the output current. The measured bare work function during the first 2000 h, however, was the same as the initial value, 4.9 eV, which is a typical value for polycrystalline rhenium. Between 2000 and 9000 h of life test, the output continued to degrade. Diagnostic work function measurements indicate the formation of patches on the electrodes. Also, an insensitivity of output current to cesium reservoir temperatures was observed. Effects of the collector temperature on the output remained qualitatively unchanged. Since emitter poisoning was suspected as a cause for the output degradation at about 3500 h, the emitter was flashed twice by increasing emitter temperature to 2200 K for 2 min in an attempt to vaporize emitting surface impurities. Immediately after the flashing, the output power increased by approximately 10 %, but it decreased with time to the original level within 24 h. Thus, diffusion of the uranium nitride through the rhenium and contamination of electrode surfaces are suspected, although the converter is still operating at 2.5 W/cm^2 at 0.5 V with an emitter temperature of 1900 K.

V. CONCLUSIONS

Uranium nitride appears unsuitable for thermionic applications at temperatures of 1900 K or above because of grain boundary penetration through tungsten and rhenium. This penetration produces emitter cracks, electrode contamination, and a reduction in thermionic performance.

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4. Shimada, K., and Cassell, P. L., Evaluation of Converters Fueled with Uranium Nitride, Technical Memorandum 33-489, Jet Propulsion Laboratory, Pasadena, Calif., July 30, 1971.
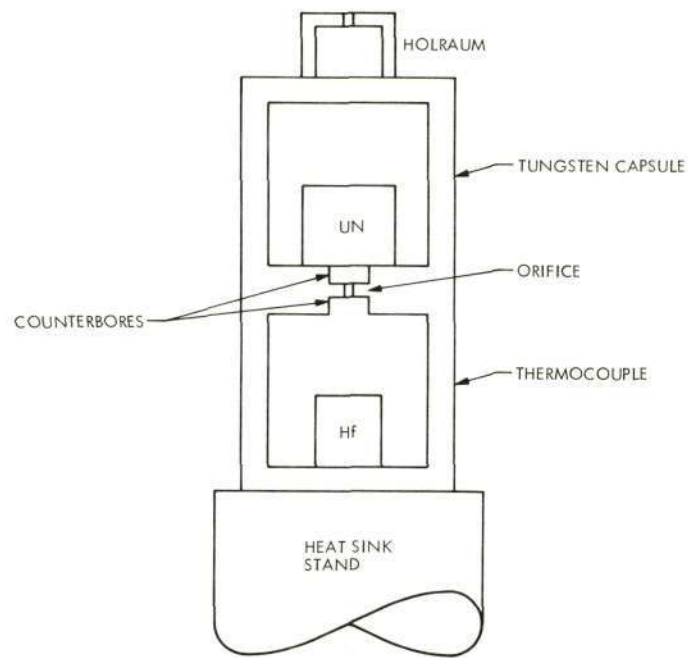
Fig. 1. Schematic of uranium nitride/
tungsten thermal gradient
compatibility test capsule

Fig. 2. Metallographic section of
uranium nitride after test

UPPER
COUNTERBORE →

UN →

TUNGSTEN →
WEB AREA

AREA SHOWN
IN FIG. 4 →

0.4 mm

0.02 in.
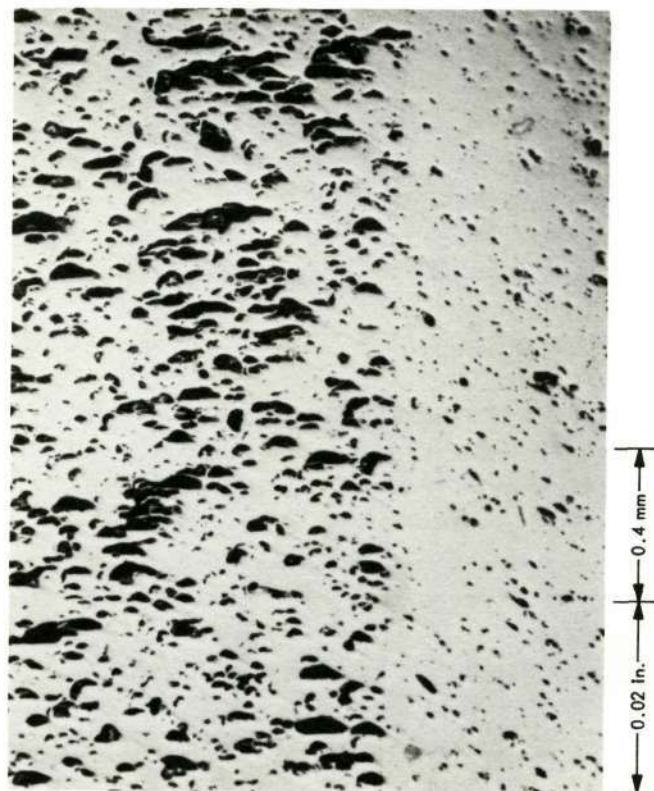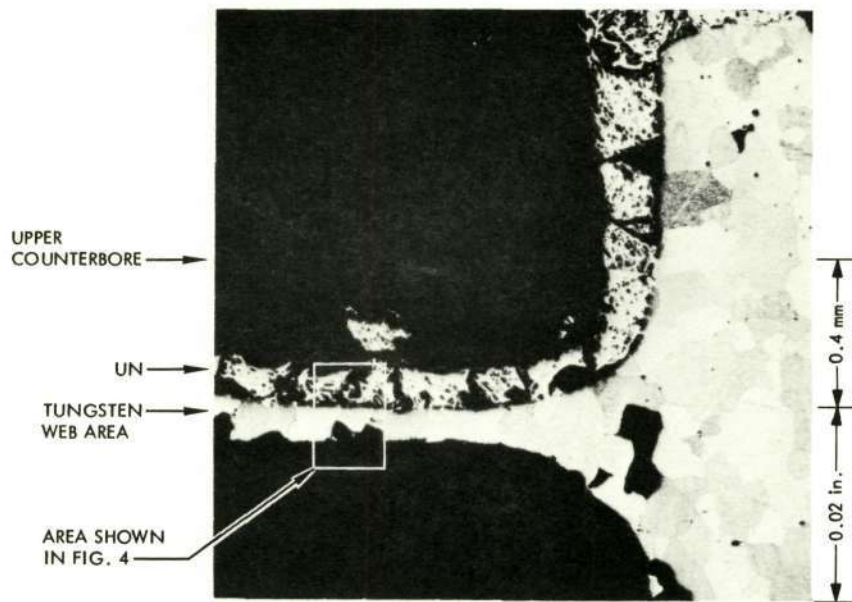
Fig. 3.   Uranium nitride redistribution into orifice
hole counterbore

← UN

UN IN GRAIN
BOUNDARY

0.04 mm

0.002 in.
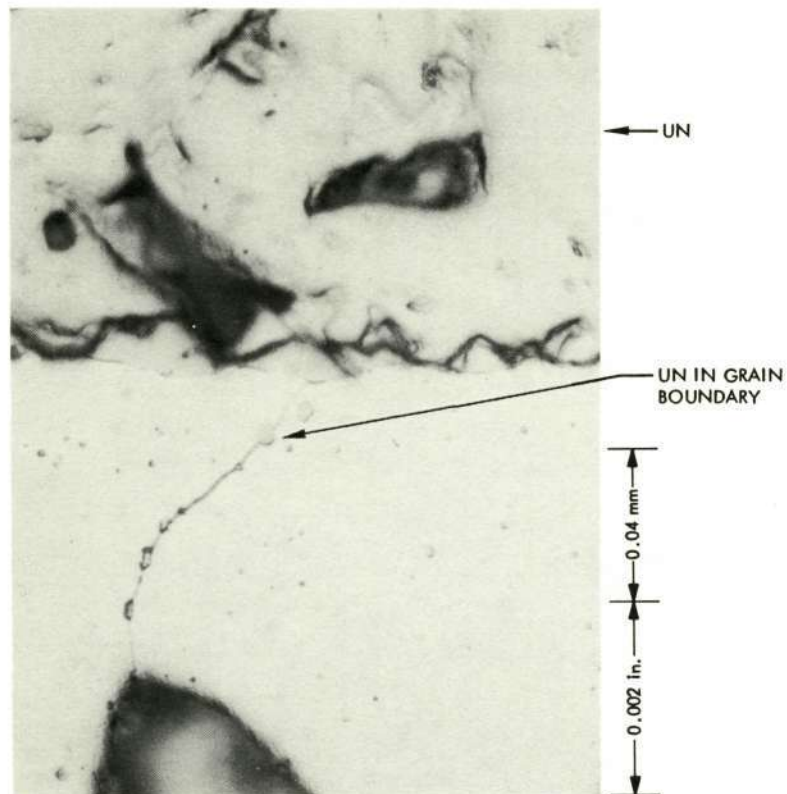
Fig. 4.   Uranium nitride penetration into
tungsten grain boundaries
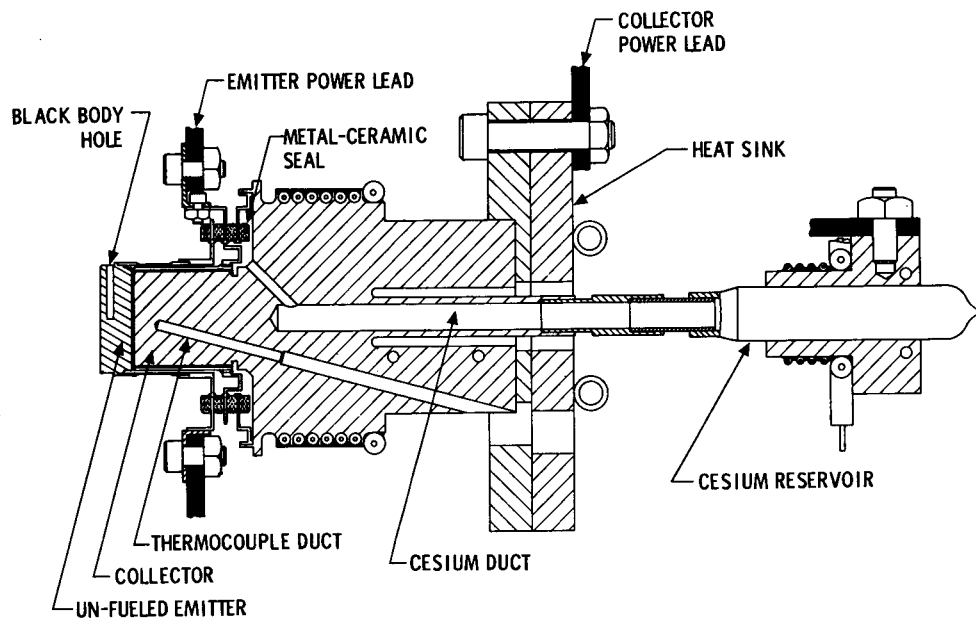
Fig. 5. Thermionic converter schematic
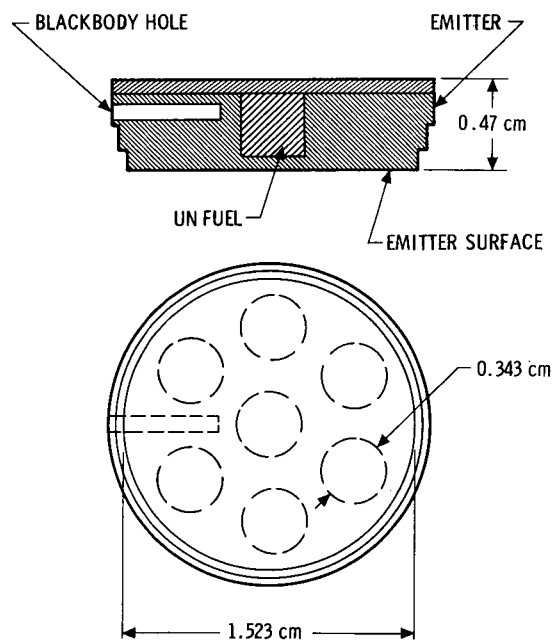
Fig. 6. Emitter schematic
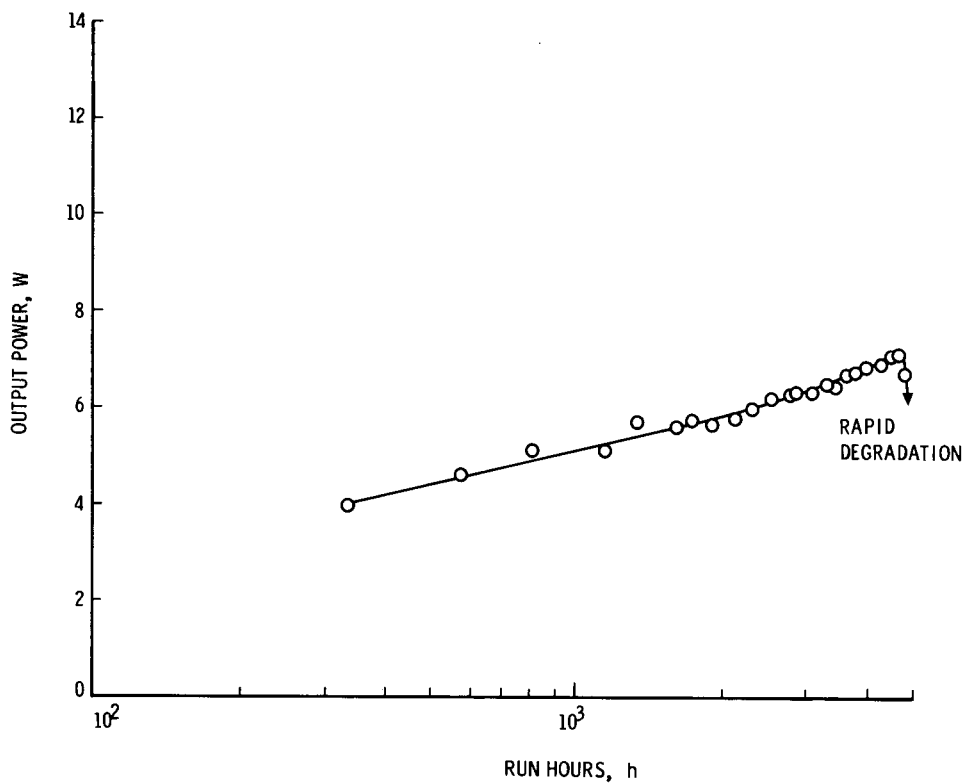
Fig. 7. Life test results, uranium nitride/tungsten emitter converter
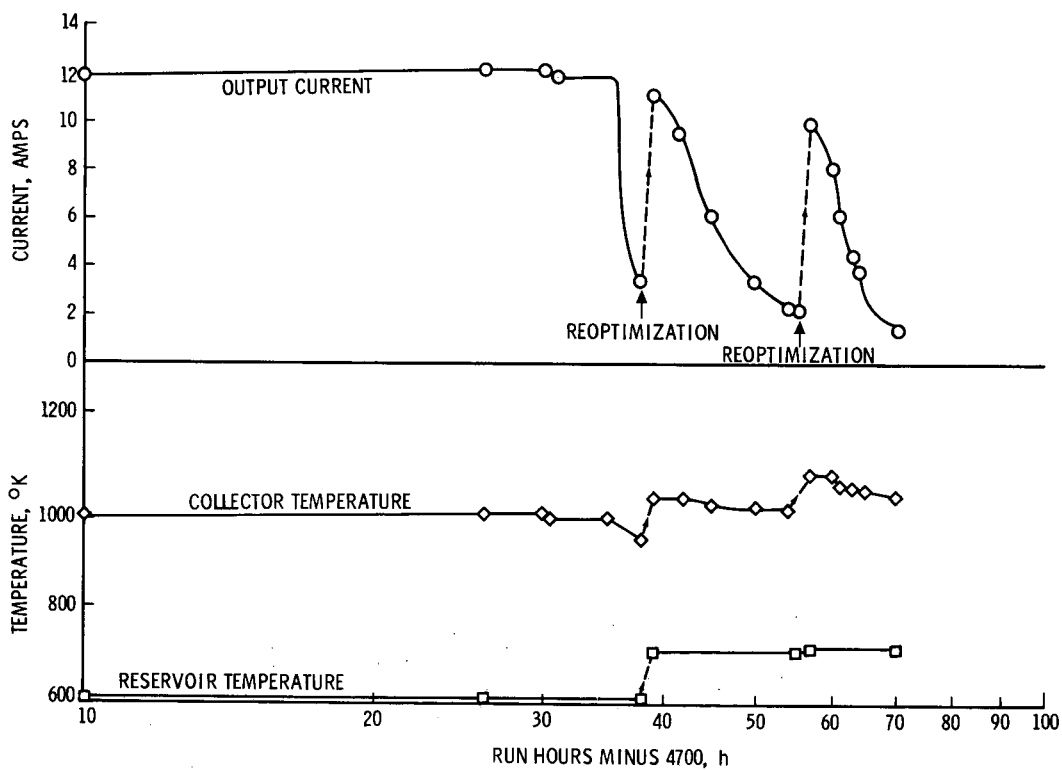
Fig. 8. Converter degradation detail

Fig. 9.   Uranium nitride/tungsten
emitter after test
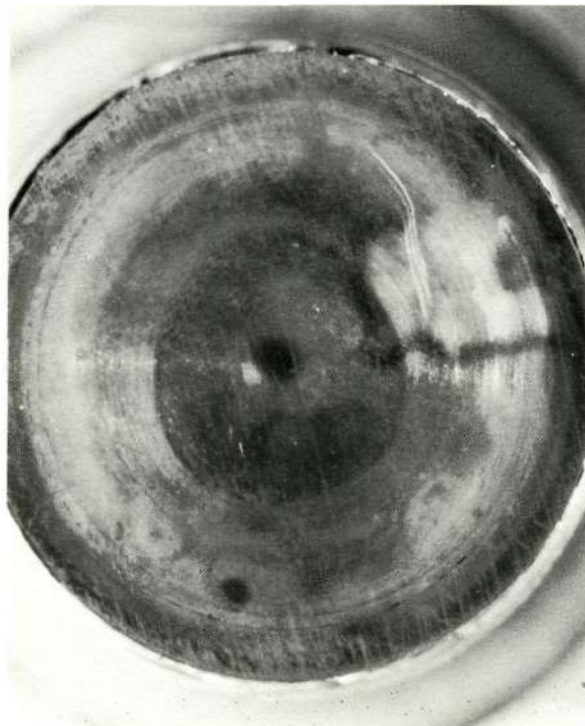
Fig. 10.   Uranium nitride/tungsten
converter collector
after test

UN ⟶

AREA SHOWN
IN FIG. 12 ⟶

TUNGSTEN ⟶

EMITTING
SURFACE ⟶

0.2 mm

0.01 in.
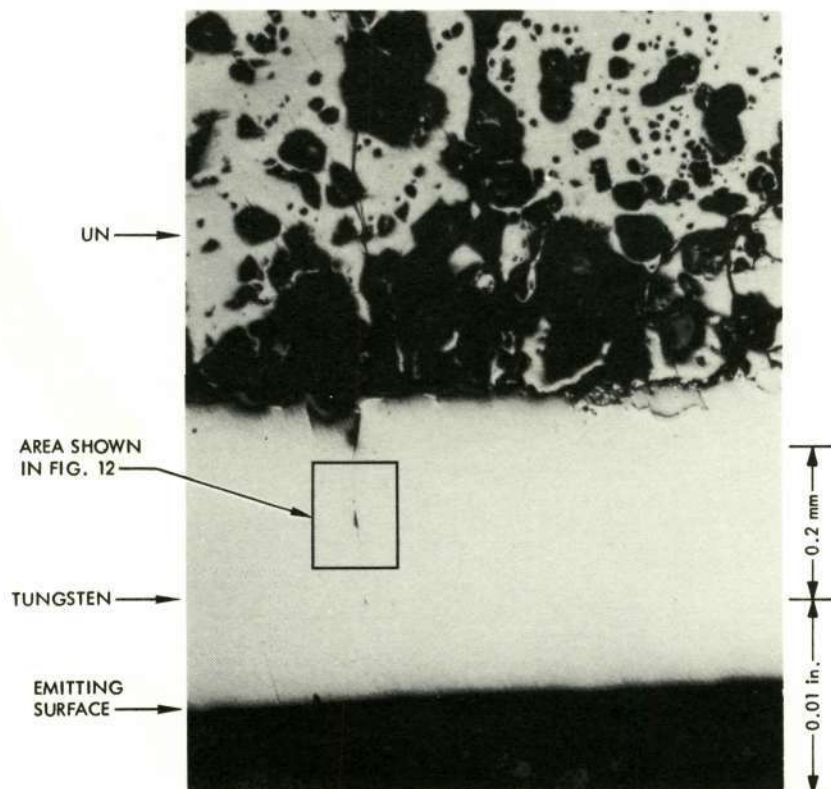
Fig. 11. Metallographic section of uranium nitride/
tungsten emitter, fuel tungsten interface
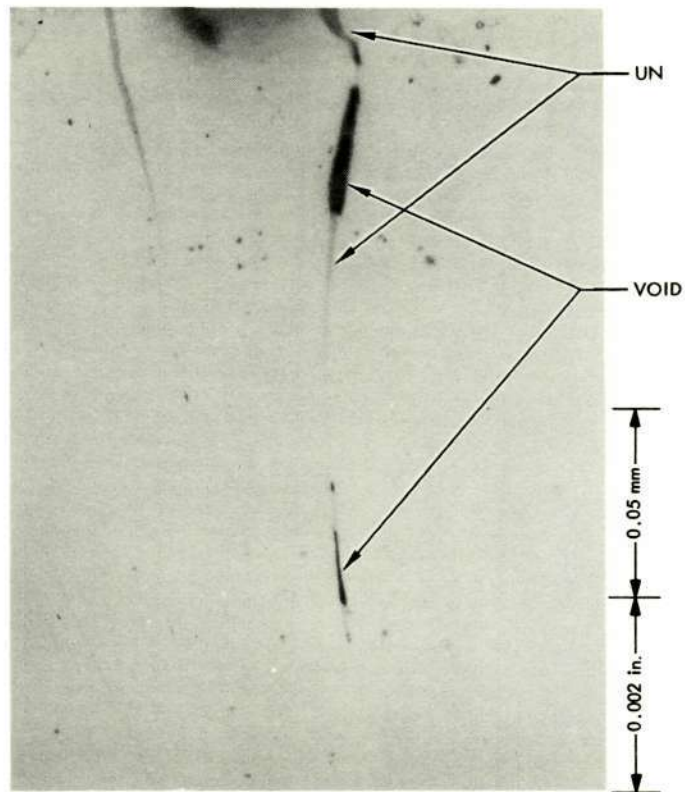
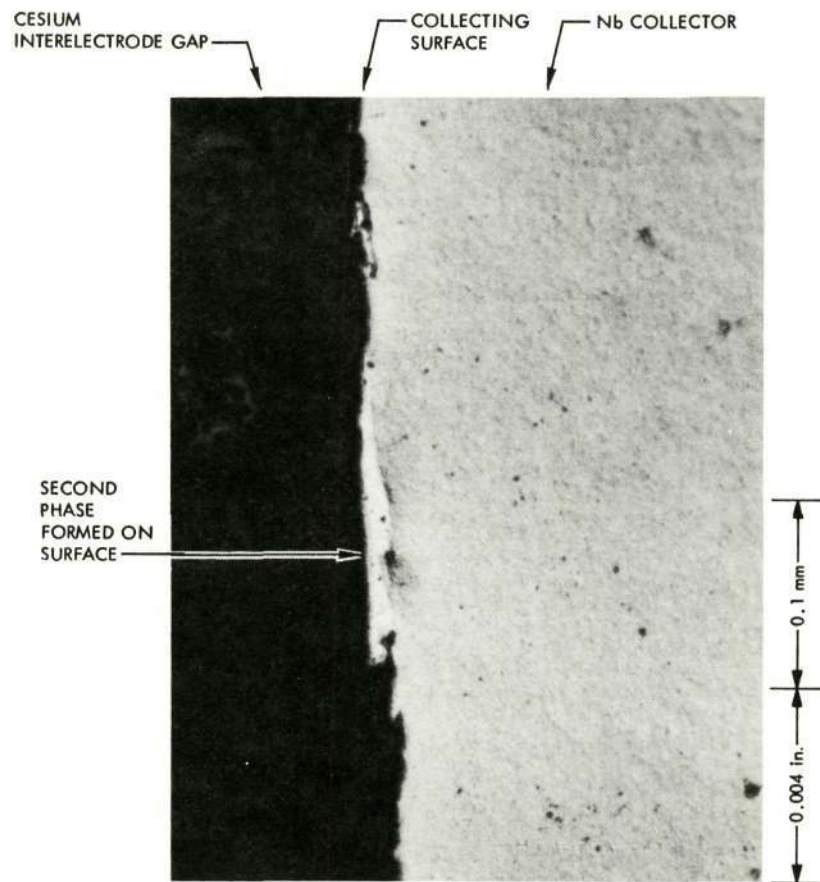Fig. 12. Metallographic section of uranium nitride/tungsten emitter, UN penetration into tungsten

CESIUM
INTERELECTRODE GAP

COLLECTING
SURFACE

Nb COLLECTOR

SECOND
PHASE
FORMED ON
SURFACE

0.1 mm

0.004 in.

Fig. 13. Metallographic section of uranium
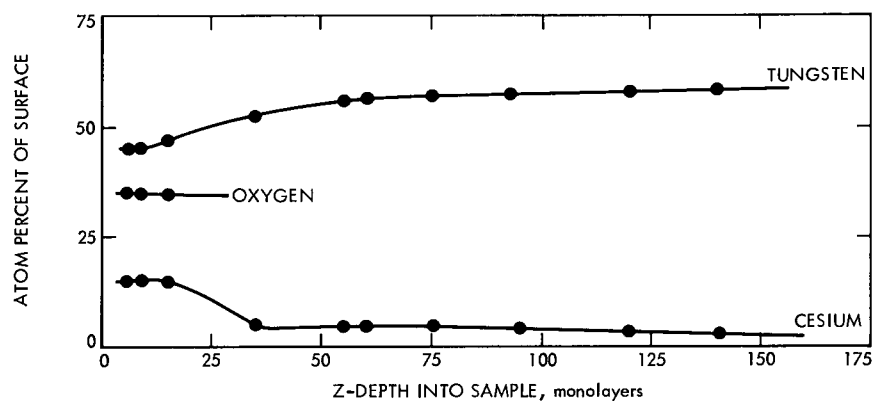nitride/tungsten converter
collector

Fig. 14. Depth profile of emitter showing abundance of major constituents in atomic percent coverage of the analyzed surface as a function of depth into the sample (Z) in monolayers
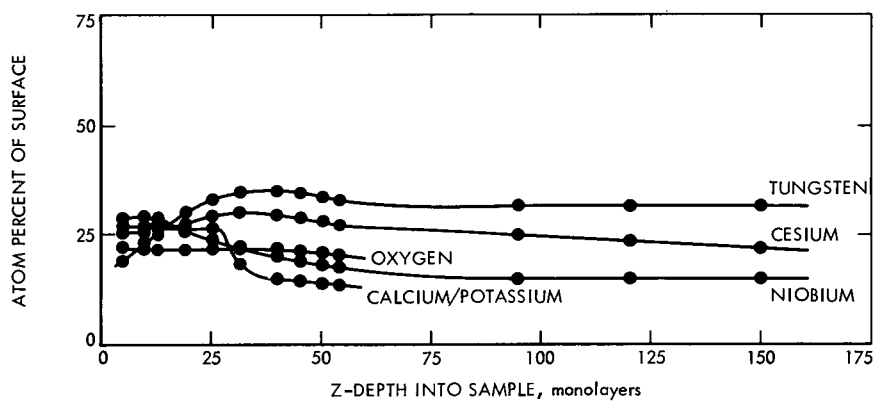

Fig. 15. Depth profile of collector showing abundance of major constituents in atomic percent coverage of the analyzed surface as a function of depth into the sample (Z) in monolayers
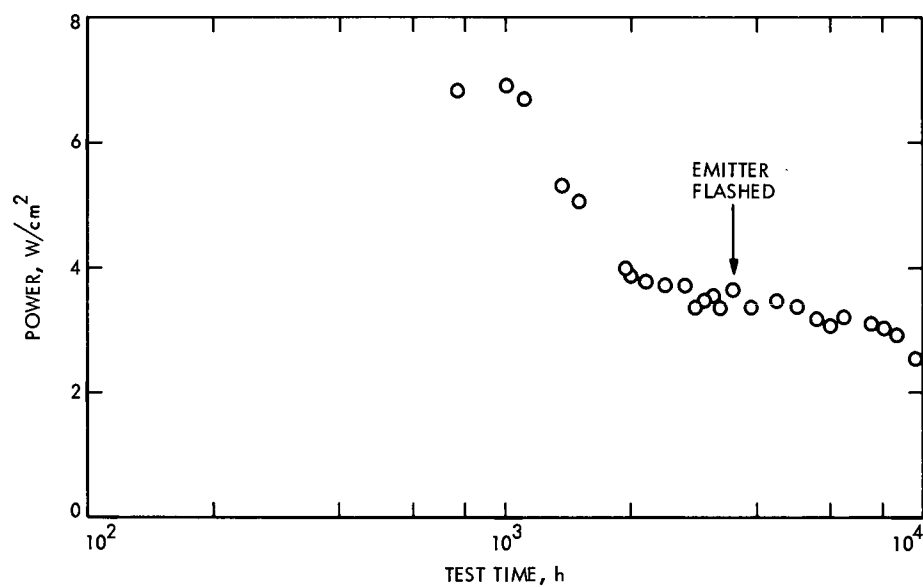
Fig. 16. Life test results, uranium nitride/rhenium emitter converter