G. H. Lee January 19, 1965

R. K. Sharp

BEST AVAILABLE COPY

PATENT CLEARANCES

I have given patent clearance to the following documents.

Number	Title
HW-SA-3724 (Copy enclosed)	"Current Methods in Plutonium Fuel Fabrication", a 16 mm motion picture in color and sound. Remarks: Discloses the subject matter of HWIR-377 - AEC Case S-16,710; HWIR-1512 - AEC Case No. S-27,336; and HWIR-1745 - AEC Case No. S-31,328. Patent applications have been filed on AEC Cases S-16,710 and S-27,336. AEC Case S-31,328 has been inactivated.
HW-81602 (Copy enclosed)	"Ceramics Research and Development Quarterly Report - July - September 1964" Remarks: Discloses the subject matter of HWIR-128 - AEC Case S-24,036; HWIR-1533 - AEC Case S-27,443; HWIR-1616 - AEC Case S-28,267; HWIR-1644 - AEC Case S-29,355; and HWIR-1745 - AEC Case S-31,328. AEC Case S-24,036 has been combined with AEC Case S-22,961 (HWIR-1209) and patented. AEC Cases S-27,443 and S-31,328 have been inactivated. Patent applications have been filed on AEC Cases S-28,267 and S-29,355.

RKS:eg

Enclosures:
HW-SA-3724
HW-81602

Reviewed and Approved for
Public Release by the Hanford
Declassification Project
W. F. Nicaise PNNL ADD
4-5-2000 Date

TO: Maurine Sheridan

December 28, 1964

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE CERAMICS RESEARCH AND DEVELOPMENT QUARTERLY REPORT JULY - SEPTEMBER 1964	DOCUMENT NUMBER HW-31602
AUTHOR	
PROPOSED DISTRIBUTION TID-4500	

PATENT REVIEW

☒ NO OBJECTION TO PROPOSED DISTRIBUTION

☐ DOES NOT DISCLOSE AN INVENTION.

☒ DISCLOSES THE SUBJECT MATTER OF HWIR– 1287, 1533, 1616, 1644, 1745

☐ DO NOT RELEASE FOR UNRESTRICTED EXTERNAL DISTRIBUTION.

☐ DISCLOSES POSSIBLE INVENTION(S) ON WHICH NO HWIR HAS BEEN FILED.

☐ DISCLOSES SUBJECT MATTER OF HWIR–

REMARKS: HWIR-1287 combined with HWIR-1205 and patented. HWIR-1533 and HWIR-1745 have been dropped. Patent applications have been filed on HWIR-1616 and HWIR-1644.

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION.

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS:

cc: HWIR Files
Publications File

Robert Keith Sharp
PATENT ATTORNEY
COUNSEL'S OFFICE

BD-7000-010 (4-63) AEC-GE RICHLAND, WASH.

G. H. Lee, Chief
Chicago Patent Group

February 24, 1965

R. K. Sharp, Patent Attorney
Chicago Patent Group

HWIR-1287 - AEC CASE S-24,036
HWIR-1533 - AEC CASE S-27,443
HWIR-1616 - AEC CASE S-28,267
HWIR-1644 - AEC CASE S-29,355
HWIR-1745 - AEC CASE S-31,328

I have given patent clearance on the following document, which you have received under standard distribution. The subject matter of the above cases is disclosed.

HW-31602 - CERAMICS RESEARCH AND DEVELOPMENT QUARTERLY REPORT
JULY - SEPTEMBER 1964

HWIR-1287 - AEC Case S-24,036 has been combined with HWIR-1209 - AEC Case S-22,961 and patented.

HWIR-1533 - AEC Case S-27,443 has been dropped.

Patent applications have been filed on the other cases.

Material directed to HWIR-1735 - AEC Case S-31,296 was refused clearance and removed before printing.

RKS:eg

cc: RC Ennis
HWIR Files

54-3000-290(8-62)

GENERAL ELECTRIC
COMPANY

RICHLAND, WASHINGTON . . . TELEPHONE AREA CODE 509, 942-1111
Extension 3601

HANFORD
ATOMIC
PRODUCTS
OPERATION
3760 Bldg., 300 Area

November 17, 1964

Mr. George H. Lee, Chief
Chicago Patent Group
U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

bcc: HWIR Files
Publications File
Record Copy
LB

Subject: RELEASE OF DOCUMENT

HWIR-	AEC CASE NO.
1533	S-27,443
1644	S-29,355
1732	S-31,293
1745	S-31,323

Dear Mr. Lee:

In accordance with your letters of April 8, 1960 and July 18, 1961, I have given patent clearance for distribution or publication of the following document, a copy of which is enclosed:

Document Number: HW-82601

Title: "Ceramics Research and Development Operation Quarterly Report" - April - June, 1964.

Author:

Type of Distribution: TID-4500

The above invention report(s) is (are) involved.

Remarks: A patent application has been filed on AEC Case S-29,355. The other cases have been dropped.

Very truly yours,

Robert Keith Sharp
Patent Attorney

RKS:eg
Enclosure

cc: Roland A. Anderson - USAEC-HDQ (w/encl.)

TO: Maurine Sheridan

November 17, 1964

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE CERAMICS RESEARCH AND DEVELOPMENT OPERATION QUARTERLY REPORT APRIL - JUNE, 1964	DOCUMENT NUMBER HW-31601
AUTHOR	
PROPOSED DISTRIBUTION TID-4500	

PATENT REVIEW

☒ NO OBJECTION TO PROPOSED DISTRIBUTION

☐ DOES NOT DISCLOSE AN INVENTION.

☒ DISCLOSES THE SUBJECT MATTER OF HWIR- 1732, 1745, 1533, 1644

☐ DO NOT RELEASE FOR UNRESTRICTED EXTERNAL DISTRIBUTION

☐ DISCLOSES POSSIBLE INVENTION(S) ON WHICH NO HWIR HAS BEEN FILED.

☐ DISCLOSES SUBJECT MATTER OF HWIR-

REMARKS: A patent application has been filed on HWIR-1644. The other cases have been dropped.

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION.

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS:

cc: HWIR Files and HWIR-1735
Publications File

Robert Keith Sharp
PATENT ATTORNEY
COUNSEL'S OFFICE

54-3000-290 (8-62)

GENERAL ELECTRIC
COMPANY

RICHLAND, WASHINGTON . . . TELEPHONE AREA CODE 509, 942-1111
Extension 3601

HANFORD
ATOMIC
PRODUCTS
OPERATION
3760 Bldg., 300 Area

NOV 10 1964

bcc: HWIR-1533
HWIR-1644
Publications File
Record Copy
LB

Mr. George H. Lee, Chief
Chicago Patent Group
U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

Subject: RELEASE OF DOCUMENT

HWIR-	AEC CASE NO.
1533	S-27,443
1644	S-29,355

COPY

Dear Mr. Lee:

In accordance with your letters of April 8, 1960 and July 18, 1961, I have given patent clearance for distribution or publication of the following document, a copy of which is enclosed:

Document Number: None

Title: "Plutonium R&D Newsletter - Reporting Results for July, August and September, 1964 - Issue No. 7"

Author: J. V. McMaster

Type of Distribution: Special

The above invention report(s) ~~is~~ (are) involved.

Remarks: AEC Case S-27,443 has been dropped. A patent application has been filed on AEC Case S-29,355.

Very truly yours,

Robert Keith Sharp
Patent Attorney

RKS:eg
Enclosure

cc: Roland A. Anderson - USAEC-HDQ (w/encl.)

TO: Jack McMaster

November 6, 1964

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE

PLUTONIUM R&D NEWSLETTER - Reporting Results for July, August and September, 1964 - ISSUE NO. 7

DOCUMENT NUMBER

None

AUTHOR

PROPOSED DISTRIBUTION

PATENT REVIEW

☒ NO OBJECTION TO PROPOSED DISTRIBUTION

- ☐ DOES NOT DISCLOSE AN INVENTION.
- ☒ DISCLOSES THE SUBJECT MATTER OF HWIR- 1533, 1644

☐ DO NOT RELEASE FOR UNRESTRICTED EXTERNAL DISTRIBUTION.

- ☐ DISCLOSES POSSIBLE INVENTION(S) ON WHICH NO HWIR HAS BEEN FILED.
- ☐ DISCLOSES SUBJECT MATTER OF HWIR-

REMARKS: HWIR-1533 has been dropped. A patent application has been filed on HWIR-1644.

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION.

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS:

cc: HWIR Files
Publications File

PATENT ATTORNEY
COUNSEL'S OFFICE

TO: K. Green

October 19, 1964

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE CERAMICS RESEARCH AND DEVELOPMENT QUARTERLY REPORT JULY - SEPTEMBER 1964	DOCUMENT NUMBER HW-81602
AUTHOR	
PROPOSED DISTRIBUTION TID-4500	

PATENT REVIEW

☒ NO OBJECTION TO PROPOSED DISTRIBUTION EXCEPT AS NOTED BELOW

  ☐ DOES NOT DISCLOSE AN INVENTION.

  ☒ DISCLOSES THE SUBJECT MATTER OF HWIR- 1287, 1533, 1616, 1644, 1745

☒ DO NOT RELEASE FOR UNRESTRICTED EXTERNAL DISTRIBUTION.

  Hampson & Robinson - UO_2 Graphite Dispersions

  ☒ DISCLOSES POSSIBLE INVENTION(S) ON WHICH NO HWIR HAS BEEN FILED.

  Allen - Inverted Cluster Fuel Element

  ☒ DISCLOSES SUBJECT MATTER OF HWIR- 1735

REMARKS: HWIR-1287 combined with 1209 and patented. HWIR-1533 has been dropped. Patent applications filed on HWIR-1616, HWIR-1644, and HWIR-1745. Awaiting AEC action on HWIR-1735. (Clearance has been requested.)

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION.

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS:

cc: DR de Halas
RJ Lobsinger
HWIR Files
To be reported file

ORIGINAL SIGNED BY

Robert Keith Sharp
PATENT ATTORNEY
COUNSEL'S OFFICE

BD-7000-010 (4-63) AEC-GE RICHLAND, WASH.

TO: Jack Brown

October 5, 1964

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE CERAMIC RESEARCH AND DEVELOPMENT OPERATION QUARTERLY REPORT APRIL-JUNE, 1964	DOCUMENT NUMBER HW-81601
AUTHOR (Staff)	
PROPOSED DISTRIBUTION TID-4500	

PATENT REVIEW

☒ NO OBJECTION TO PROPOSED DISTRIBUTION **EXCEPT AS NOTED**

- ☐ DOES NOT DISCLOSE AN INVENTION.
- ☒ DISCLOSES THE SUBJECT MATTER OF HWIR- 1732, 1745, 1533, 1644

☒ DO NOT RELEASE FOR UNRESTRICTED EXTERNAL DISTRIBUTION

Freshley - PRTR Fuel Element Development

- ☐ DISCLOSES POSSIBLE INVENTION(S) ON WHICH NO HWIR HAS BEEN FILED.
- ☒ DISCLOSES SUBJECT MATTER OF HWIR- 1735

REMARKS: HWIR-1732 has been dropped. Clearance of HWIR-1745 received from AEC. HWIR-1533 has been dropped. Patent application has been filed on HWIR-1644. AEC is awaiting tests before acting on HWIR-1735.

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION.

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS:

cc: HWIR Files
DR de Halas
Publications File
To be Reported File

Robert Keith Sharp
PATENT ATTORNEY
COUNSEL'S OFFICE

BD-7000-010 (4-63) AEC-GE RICHLAND, WASH.

UNITED STATES
ATOMIC ENERGY COMMISSION
WASHINGTON 25, D.C.

IN REPLY REFER TO:

GCP:RAA

February 11, 1963

Mr. Robert Keith Sharp
Patent Attorney
General Electric Company
3760 Building, 300 Area
Richland, Washington

SUBJECT: AEC CASE S-27,443 (HWIR NO. 1533)

Dear Mr. Sharp:

There was transmitted to this office with Mr. Lee's memorandum of August 9, 1962, your letter and the above HWIR disclosure. This office has determined that it is not advisable for the Government to proceed with the preparation of a patent application on this case since the thermal treatment of uranium dioxide in the presence of hydrogen, steam, and moist gases is old as can be seen from: (1) the article by Arenberg and Jahn on pages 179 to 183 of volume 41 of the Journal of the American Ceramic Society; (2) NP-6667; (3) NP-8383; and (4) British Patent 844,980. All of these references are abstracted in Nuclear Science Abstracts.

Very truly yours,

Roland A. Anderson

Roland A. Anderson
Assistant General Counsel
for Patents

cc: George H. Lee, Chief
Chicago Patent Group

Note: Sent copy of this letter and Inventory Report
with all attachments to [illegible] 2/12/63

54-3000-101 (9-59)

DON'T SAY IT --- *Write It!*

TO R Keith Sharp

DATE 8/28/62

FROM WJ Anderson

Re: HW-SA-2663 & HWIR-1533

As per your 8/20/62 review, I have taken out the sections on "Removal of Impurities and Cattle C." I plan now to submit the new paper to you through proper channels. For your information, attached are the two papers - "before and after."

Thanks WJA

"SOME LEARN FROM EXPERIENCE, SOME NEVER RECOVER FROM IT"

August 20, 1962

TO: H. J. Anderson and James C. Langford

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE DETERMINATION AND CONTROL OF NITROGEN AS URANIUM NITRIDES IN FUSED URANIUM DIOXIDE (UO_2)	DOCUMENT NUMBER HW-SA-2663
AUTHOR H. J. Anderson and James C. Langford	
PROPOSED DISTRIBUTION For publication in ANALYTICAL CHEMISTRY	

PATENT REVIEW

☐ NO OBJECTION TO PROPOSED DISTRIBUTION

  ☐ DOES NOT DISCLOSE AN INVENTION.

  ☐ DISCLOSES THE SUBJECT MATTER OF HWIR-

☒ DO NOT RELEASE FOR UNRESTRICTED EXTERNAL DISTRIBUTION

  ☐ DISCLOSES POSSIBLE INVENTION(S) ON WHICH NO HWIR HAS BEEN FILED.

  ☒ DISCLOSES SUBJECT MATTER OF HWIR- 1533

REMARKS: Clearance is denied for the present by AEC. Can be cleared if section on "Removal of Impurities" and Table II are deleted.

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS:

cc: HWIR-1533
Publications File

Robert Keith Sharp
PATENT ATTORNEY
COUNSEL'S OFFICE

A-7000-012 (9-61)

HW-SA-2663
July 12, 1962

DETERMINATION OF NITROGEN AS URANIUM NITRIDES IN FUSED URANIUM DIOXIDE (UO_2)

By Harlan J. Anderson and James C. Langford

Hanford Atomic Products Operation
General Electric Company
Richland, Washington *

Introduction

In-reactor tests of UO_2 fuel elements can be abruptly terminated by cladding failures caused by excessive internal gas pressures. In fuel fabrication development studies, therefore, an accurate analysis is required of fixed or sorbed gases present in candidate fuel materials before fabrication(1). Fused UO_2 is one of several candidate ceramic fuel materials.

Brite and Anderson reported(3) the presence, ease of formation, and possible mechanism of formation of uranium nitrides in fused UO_2. Anderson also reported(4) that uranium mononitride (UN), uranium sesquinitride (U_2N_3), and uranium dinitride (UN_2) can act as copious sources of nitrogen in fused UO_2.

In our laboratories, vacuum extraction and Kjeldahl techniques are used to analyze for fixed or sorbed gas content in UO_2 samples. Past efforts to correlate nitrogen values obtained by these two analytical techniques with calculated values of prepared UO_2 samples containing known amounts of UN and UN_2 have not been successful. Nitrogen values for samples of commercially fused UO_2 also have represented areas of disagreement between vendor and our laboratories. Because of inconsistency among analyses, study of analytical techniques was undertaken and completed.

A new analytical technique was developed and successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused UO_2.

---

* Work performed for the U. S. Atomic Energy Commission under Contract AT(45-1)-1350.

HW-SA-2663
July 12, 1962

Abstract

A new Kjeldahl digestion technique that uses a mixture of 1:1 diluted hydrochloric acid with additions of copper selenate and hydrofluosilicic acid was successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused uranium dioxide (UO_2). Usual digestion techniques and vacuum extraction at 1000°C were inadequate for analysis of all uranium nitride species present in (fused) UO_2.

General Approach

Our observations and data showed that the bulk of the nitrogen present in fused UO_2 is in the form of uranium nitrides. The Kjeldahl technique, therefore, appeared to be the best analytical approach. Dissolution of UO_2 samples was considered of primary importance.

Reagents that might be effective in dissolving UO_2 have been reported(2). Determinations of nitrogen in UO_2 has been reported(7) by Bennett using an oxidizing alkaline fusion followed by measurement of the volume of released nitrogen. Generally, the analytical approach for nitrogen determination was the Kjeldahl method with modifications of digestion techniques(8). A note(5) on a method for the determination of nitrogen content in uranium nitrides was important since these nitrogen species were identified as present in our fused UO_2. Several digestion methods were tested using 200 milligrams (mg) samples of -100 mesh UO_2. Two prepared samples consisting of UN in UO_2 and UN_2 in UO_2 were used for each method.

Existing routine methods used in our laboratories yielded poor results on both UN and UN_2 content in UO_2 prepared samples. One method consisted of sample digestion in concentrated HCl, or variations of diluted HCl with additions of zinc metal for generation of active hydrogen. Another method was a sample digestion in $HClO_4$ and H_2O_2 or Na_2O_2.

Only nitrogen values obtained by digestion of the samples in a mixture consisting of 1:1 diluted HCl with additions of copper selenate and hydrofluosilicic acid were acceptable for both UN in UO_2 and UN_2 in UO_2 prepared samples.

Apparatus and Reagents

Kjeldahl equipment, conventional laboratory glassware, and reagent grade chemicals were used unless otherwise stated.

A NaOH solution was made by dissolving 680 grams of NaOH in two liters of distilled water. Devarda's alloy, 0.5 grams, was added. Solutions were boiled until the volume was reduced to 1.8 liters(9). A mixed indicator of brom cresol green(6) and methyl red was used. Methyl red indicator was used to increase the sensitivity of the end point direction.

Procedure

Weigh out about 200 mg. of -100 mesh UO_2 sample into a 50 ml. Erlenmeyer flask. Record actual weight. Then, add 25 ml. of 1:1 HCl and 2 ml. of H_2SiF_6. Do not cover, but heat just below boiling for about 30 minutes. Add about 200 mg. of copper or potassium selenate. Digest until solution is complete.

Transfer the cooled sample solution to Kjeldahl distillation equipment and add 25 ml. NaOH solution. Distill and collect the condensate in a 50 ml. Erlenmeyer flask containing the mixed indicator solution and 5 ml. of 4% boric acid solution(6). Adjust the heat input so that about 20 ml. of condensate will be collected in five minutes. The boric acid solution need not be accurately measured(9).

Titrate the collected ammonia (ammonium borate) with a standard acid of 0.005 normality (N). Make a blank determination using the same amount of reagent as in the sample determination.

Calculate nitrogen content by the following formula:

$$\text{parts per million (ppm) N (nitrogen)} = \frac{(\text{ml Titration} - \text{ml Blank}) \times N \times 14.007 \times 1000}{\text{Grams Sample}}$$

Duplicate results should agree within 0.3% relative.

Results and Discussion

The preliminary work was performed on two samples consisting of UN in UO_2 and UN_2 in UO_2. Table 1 shows that of the several digestion techniques available for analyzing nitrogen as uranium nitrides in UO_2, only the recommended technique gave complete recovery of the nitrogen. An important feature of this digestion technique is the essential action of the selenate ion, described by Lathouse et al(5).

Past efforts to correlate nitrogen values obtained by vacuum extraction and by Kjeldahl techniques were not successful on either commercial samples or prepared samples (Table I) containing known amounts of UN and UN_2 in UO_2.

An analysis of results indicated that the analytical techniques used were biased toward particular species of uranium nitride. Some digestion procedures using Kjeldahl techniques gave good values for fused UO_2 containing UN, but were erratic for UN_2 in UO_2. In contrast, the vacuum extraction technique at 1000°C gave good results for UN_2 and U_2N_3, but low results for UN in UO_2. UN is reportedly stable in vacuum to about 1700°C.

Vacuum extraction techniques, of course, remain quite useful for measurements of sorbed gases that are released from UO_2 at the generally used 1000°C extracting temperature. But for fused UO_2 that contains UN or other high temperature stable compounds, a new, high vacuum, high temperature technique is needed.

We have modified high temperature vacuum fusion equipment to permit operating temperatures to 2000°C. Ordinarily a graphite crucible and graphite heat shield is used. Graphite reduces UO_2 at 2000°C. That reaction may be useful as an analytical technique for determining oxygen-to-uranium atom ratios. Use of a tungsten crucible and tungsten powder for a heat shield in our vacuum fusion equipment appears to be a promising analytical technique for high temperature compounds such as UN in UO_2.

Conclusions

Existing routine digestion techniques for Kjeldahl analysis, and vacuum extraction techniques for analysis of all uranium nitride species present in fused UO_2, were inadequate. A satisfactory technique was developed and successfully used.

From our studies on the ease of formation of uranium nitrides in fused UO_2, we conclude that uranium nitride formations may also occur in UO_2 powders and pellets that are sintered in cracked ammonia. Use of pure hydrogen rather than cracked ammonia in UO_2 sintered processes is recommended.

Acknowledgement

The authors thank both Mrs. I. S. Paret and Mrs. A. D. Couch for performing many developmental determinations. Thanks are also due to D. W. Brite, and D. R. de Halas and W. E. Roake for their helpful criticisms and suggestions.

Literature Cited

(1) Anicetti, R. J., Hauth, J. J. "Specifications for Fused Uranium Dioxide", HW-61653 Rev. 1. February 15, 1961.

(2) Belle, J. (Ed.). "Uranium Dioxide" Properties and Nuclear Application, (USAEC, 1961)

(3) Cadwell, J. J. "Quarterly Progress Report", Fuels Development Operation, HW-72346 October, November, December, 1961 (Classified)

(4) Cadwell, J. J., "Quarterly Progress Report", Fuels Development Operation, HW-74377 April, May, June, 1962 (Classified)

(5) Lathouse, Joan, Huber, F. E. Jr., Chase, B. L. Analytical Chemistry, Vol. 31, December 9, 1959, page 1606-7

(6) Pierce W. C., Haenisch, E. L., "Quantitative Analysis", 2nd ed., page 123 Wiley, New York, 1940

(7) Popper, P., (Ed.) Special Ceramics, Proceedings of a Symposium, British Ceramic Research Association, Heywood, London, 1960

(8) Rodden, C. J., "Analytical Chemistry of the Manhattan Project", page 208, McGraw Hill, New York, 1950

(9) Winkler, L. W., Z. angew Chem., 26, page 231 (1913)

TABLE I. Analysis of Nitrogen as Uranium Nitrides in Fused UO_2

	Nitrogen (ppm)				
Sample	1	2	3[b]	4	Theoretical
UN (in UO_2)	690	890	1310	250	1340
UN_2 (in UO_2)[a]	540	1450	1220	690	1250

Digestion Methods (Kjeldahl Techniques)

1. Hydrochloric Acid
2. Perchloric Acid and Hydrogen Peroxide
3. 1:1 HCl with additions of (copper) selenate and hydrofluosilicic acid.
4. Vacuum Extraction at 1000°C with mass spectrometric analysis of gases.

[a] Some U_2N_3 possible in sample

[b] New Digestion Technique

HW-SA-2663
July 12, 1962

DETERMINATION AND CONTROL OF NITROGEN AS URANIUM NITRIDES IN FUSED URANIUM DIOXIDE (UO_2)

BY Harlan J. Anderson and James C. Langford

Hanford Atomic Products Operation
General Electric Company
Richland, Washington*

Introduction

In-reactor tests of UO_2 fuel elements can be abruptly terminated by cladding failures caused by excessive internal gas pressures. In fuel fabrication development studies, therefore, an accurate analysis is required of fixed or sorbed gases present in candidate fuel materials before fabrication(1). Fused UO_2 is one of several candidate ceramic fuel materials.

Brite and Anderson reported(3) the presence, ease of formation, and possible mechanism of formation of uranium nitrides in fused UO_2. Anderson also reported(4) that uranium mononitride (UN), uranium sesquinitride (U_2N_3), and uranium dinitride (UN_2) can act as copious sources of nitrogen in fused UO_2.

In our laboratories, vacuum extraction and Kjeldahl techniques are used to analyze for fixed or sorbed gas content in UO_2 samples. Past efforts to correlate nitrogen values obtained by these two analytical techniques with calculated values of prepared UO_2 samples containing known amounts of UN and UN_2 have not been successful. Nitrogen values for samples of commercially fused UO_2 also have represented areas of disagreement between vendor and our laboratories. Because of inconsistency among analyses, study of analytical techniques was undertaken and completed.

A new analytical technique was developed and successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused UO_2.

---

* Work performed for the U. S. Atomic Energy Commission under Contract AT(45-1)-1350.

HW-SA-2663
July 12, 1962

Abstract

A new Kjeldahl digestion technique that uses a mixture of 1:1 diluted hydrochloric acid with additions of copper selenate and hydrofluosilicic acid was successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused uranium dioxide (UO_2). Usual digestion techniques and vacuum extraction at 1000°C were inadequate for analysis of all uranium nitride species present in (fused) UO_2. An important adjunct to these studies showed that high nitrogen levels in UO_2 can be reduced to acceptable levels by heat treating bulk UO_2 supplies at 1750°C in moist hydrogen.

General Approach

Our observations and data showed that the bulk of the nitrogen present in fused UO_2 is in the form of uranium nitrides. The Kjeldahl technique, therefore, appeared to be the best analytical approach. Dissolution of UO_2 samples was considered of primary importance.

Reagents that might be effective in dissolving UO_2 have been reported(2). Determinations of nitrogen in UO_2 has been reported(7) by Bennett using an oxidizing alkaline fusion followed by measurement of the volume of released nitrogen. Generally, the analytical approach for nitrogen determination was the Kjeldahl method with modifications of digestion techniques(8). A note(5) on a method for the determination of nitrogen content in uranium nitrides was important since these nitrogen species were identified as present in our fused UO_2. Several digestion methods were tested using 200 milligrams (mg) samples of -100 mesh UO_2. Two prepared samples consisting of UN in UO_2 and UN_2 in UO_2 were used for each method.

Existing routine methods used in our laboratories yielded poor results on both UN and UN_2 content in UO_2 prepared samples. One method consisted of sample digestion in concentrated HCl, or variations of diluted HCl with additions of zinc metal for generation of active hydrogen. Another method was a sample digestion in $HClO_4$ and H_2O_2 or Na_2O_2.

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Duplicate results should agree within 0.3% relative.

Results and Discussion

The preliminary work was performed on two samples consisting of UN in UO_2 and UN_2 in UO_2. Table 1 shows that of the several digestion techniques available for analyzing nitrogen as uranium nitrides in UO_2, only the recommended technique gave complete recovery of the nitrogen. An important feature of this digestion technique is the essential action of the selenate ion, described by Lathouse et al(5).

Past efforts to correlate nitrogen values obtained by vacuum extraction and by Kjeldahl techniques were not successful on either commercial samples or prepared samples (Table 1) containing known amounts of UN and UN_2 in UO_2.

An analysis of results indicated that the analytical techniques used were biased toward particular species of uranium nitride. Some digestion procedures using Kjeldahl techniques gave good values for fused UO_2 containing UN, but were erratic for UN_2 in UO_2. In contrast, the vacuum extraction technique at 1000°C gave good results for UN_2 and U_2N_3, but low results for UN in UO_2. UN is reportedly stable in vacuum to about 1700°C.

Vacuum extraction techniques, of course, remain quite useful for measurements of sorbed gases that are released from UO_2 at the generally used 1000°C extracting temperature. But for fused UO_2 that contains UN or other high temperature stable compounds, a new, high vacuum, high temperature technique is needed.

We have modified high temperature vacuum fusion equipment to permit operating temperatures to 2000°C. Ordinarily a graphite crucible and graphite heat shield is used. Graphite reduces UO_2 at 2000°C. That reaction may be useful as an analytical technique for determining oxygen-to-uranium atom ratios. Use of a tungsten crucible and tungsten powder for a heat shield in our vacuum fusion equipment appears to be a promising analytical technique for high temperature compounds such as UN in UO_2.

Removal of Impurities

An important adjunct to these studies showed that high nitrogen levels in fused UO_2 can be reduced to acceptable levels by heat treating bulk UO_2 materials at 1750°C in moist hydrogen.

Fused UO_2 samples originally containing UN and UN_2 were examined after heat treating at 1750°C for 12 hours in moist (1000 ppm H_2O) hydrogen. Ceramographic examination and nitrogen analysis by the new digestion technique showed removal of about 80% of the nitrogen content (Table II). Uranium nitrides (UN, U_2N_3, UN_2) can thus be substantially removed by this process.

Conclusions

Existing routine digestion techniques for Kjeldahl analysis, and vacuum extraction techniques for analysis of all uranium nitride species present in fused UO_2, were inadequate. A satisfactory technique was developed and successfully used.

From our studies on the ease of formation of uranium nitrides in fused UO_2, we conclude that uranium nitride formations may also occur in UO_2 powders and pellets that are sintered in cracked ammonia. Use of pure hydrogen rather than cracked ammonia in UO_2 sintered processes is recommended.

Acknowledgement

The authors thank both Mrs. I. S. Parent and Mrs. A. D. Couch for performing many developmental determinations. Thanks are also due to D. W. Brite, and D. R. de Halas and W. E. Roake for their helpful criticisms and suggestions.

Literature Cited

(1) Anicetti, R. J., Hauth, J. J. "Specifications for Fused Uranium Dioxide", HW-61653 Rev. 1. February 15, 1961.

(2) Belle, J. (Ed.). "Uranium Dioxide" Properties and Nuclear Application, (USAEC, 1961)

(3) Cadwell, J. J. "Quarterly Progress Report", Fuels Development Operation, HW-72346 October, November, December, 1961 (Classified)

(4) Cadwell, J. J., "Quarterly Progress Report", Fuels Development Operation, HW-74377 April, May, June, 1962 (Classified)

(5) Lathouse, Joan, Huber, F. E. Jr., Chase, B. L. Analytical Chemistry, Vol. 31, December 9, 1959, page 1606-7

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(7) Popper, P., (Ed.) Special Ceramics, Proceedings of a Symposium, British Ceramic Research Association, Heywood, London, 1960

(8) Rodden, C. J., "Analytical Chemistry of the Manhattan Project", page 208, McGraw Hill, New York, 1950

(9) Winkler, L. W., Z. angew Chem., 26, page 231 (1913)

TABLE I. Analysis of Nitrogen as Uranium Nitrides in Fused UO_2

	Nitrogen (ppm)				
Sample	1	2	3[b]	4	Theoretical
UN (in UO_2)	690	890	1310	250	1340
UN_2 (in UO_2)[a]	540	1450	1220	690	1250

Digestion Methods (Kjeldahl Techniques)

1. Hydrochloric Acid
2. Perchloric Acid and Hydrogen Peroxide
3. 1:1 HCl with additions of (copper) selenate and hydrofluosilicic acid.
4. Vacuum Extraction at 1000°C with mass spectrometric analysis of gases.

[a] Some U_2N_3 possible in sample

[b] New Digestion Technique

TABLE II. Removal of Nitrogen from Fused UO_2

Sample	Nitrogen (ppm) Before	After (H_2 Treatment) Kjeldahl[a]	After (H_2 Treatment) Vacuum Extraction - 1000°C
UN (in UO_2)	1310	265	260
UN_2 (in UO_2)	1220	230	388

[a] Using New Digestion Technique

GENERAL ELECTRIC
COMPANY

RICHLAND, WASHINGTON . . . TELEPHONE WHitehall 2-1111

HANFORD ATOMIC
PRODUCTS OPERATION

HANFORD LABORATORIES
OPERATION

September 10, 1962

Dr. L. T. Hallett, Editor
Analytical Chemistry
1155 Sixteenth Street, N. W.
Washington 6, D. C.

Dear Dr. Hallett:

DETERMINATION OF NITROGEN AS URANIUM NITRIDES IN FUSED URANIUM DIOXIDE

Attached are the required copies of our manuscript HW-SA-2663 for publication purposes.

The information, we feel, is most important to the continued progress of both national and international UO_2 fuel power programs. Both national and foreign locations have contacted me about use of our technique to provide new information on their in-reactor fuel element failures. We feel, therefore, that the information should be presented immediately for consideration and primarily for analytical personnel.

Earlier release of the information was delayed. A section of the original manuscript was removed pending possible patent application. When this information becomes available, I would like to forward a section about the control of impurities. At this time, we are in a position to present this manuscript for your consideration.

Sincerely yours,

ORIGINAL SIGNED BY
H. J. ANDERSON

H. J. Anderson
Ceramic Fuels Development
Hanford Laboratories

HJA:db

cc: JC Langford
file

bcc: EA Evans
RK Sharp

A PRIME CONTRACTOR FOR THE U.S. ATOMIC ENERGY COMMISSION

Extension 3601   3760 Bldg., 300 Area

September 12, 1962

Mr. George H. Lee, Chief
Chicago Patent Group
U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

<u>HWIR-1533 - AEC CASE S-27,443</u>

Dear Mr. Lee:

For your information, I am enclosing the re-written version of HW-SA-2663 - "Determination of Nitrogen as Uranium Nitrides in Fused UO_2" by Harlan J. Anderson and James C. Langford - referred to in my letter of August 29, 1962, to which I have given clearance.

Very truly yours,

Robert Keith Sharp
Patent Attorney

RKS:eg

Enclosure

cc: Roland A. Anderson - USAEC-HDQ.

bcc: HWIR-1533
Record Copy
Publications File
LB

September 12, 1962

TO: **Maurine Sheridan**

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE DETERMINATION OF NITROGEN AS URANIUM NITRIDES IN FUSED UO_2	DOCUMENT NUMBER HW-SA-2663

AUTHOR Harlan J. Anderson and James C. Langford

PROPOSED DISTRIBUTION For publication: ANALYTICAL CHEMISTRY JOURNAL

PATENT REVIEW

☒ NO OBJECTION TO PROPOSED DISTRIBUTION

  ☒ DOES NOT DISCLOSE AN INVENTION.

  ☐ DISCLOSES THE SUBJECT MATTER OF HWIR– ______

☐ DO NOT RELEASE FOR UNRESTRICTED EXTERNAL DISTRIBUTION

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  ☐ DISCLOSES SUBJECT MATTER OF HWIR– ______

REMARKS: Disclosure of HWIR-1533 has been eliminated.

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION.

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS: ______

cc: Publications File
HWIR-1533

Robert Keith Sharp
PATENT ATTORNEY
COUNSEL'S OFFICE

A-7000-012 (9-61)

Extension 3601   3760 Bldg., 300 Area

August 29, 1962

Mr. George H. Lee, Chief
Chicago Patent Group
U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

<u>HWIR-1533 - AEC CASE S-27,443</u>

Dear Mr. Lee:

The author has rewritten HW-SA-2663 to eliminate the disclosure relative to this invention.

Very truly yours,

Robert Keith Sharp
Patent Attorney

RKS:eg

cc: R. A. Anderson - USAEC-HDQ.

bcc: HWIR-1533
Record Copy
Publications File
LB

August 20, 1962

TO: H. J. Anderson and James C. Langford

PATENT AND LEGAL REVIEWS ON DOCUMENTS

TITLE: DETERMINATION AND CONTROL OF NITROGEN AS URANIUM NITRIDES IN FUSED URANIUM DIOXIDE (UO_2)

DOCUMENT NUMBER: HW-SA-2663

AUTHOR: H. J. Anderson and James C. Langford

PROPOSED DISTRIBUTION: For publication in ANALYTICAL CHEMISTRY

PATENT REVIEW

☐ NO OBJECTION TO PROPOSED DISTRIBUTION

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  ☐ DISCLOSES POSSIBLE INVENTION(S) ON WHICH NO HWIR HAS BEEN FILED.

  ☒ DISCLOSES SUBJECT MATTER OF HWIR- 1533

REMARKS: Clearance is denied for the present by AEC. Can be cleared if section on "Removal of Impurities" and Table II are deleted.

GENERAL LEGAL REVIEW

☒ NO LEGAL OBJECTION TO PROPOSED DISTRIBUTION.

☐ LEGAL CLEARANCE WITHHELD OR QUALIFIED.

REMARKS:

cc: HWIR-1533
Publications File

Robert Keith Sharp
PATENT ATTORNEY
COUNSEL'S OFFICE

A-7000-012 (9-61)

UNITED STATES
ATOMIC ENERGY COMMISSION
CHICAGO OPERATIONS OFFICE
9800 SOUTH CASS AVENUE
ARGONNE, ILLINOIS

August 9, 1962

Mr. Robert Keith Sharp, Patent Attorney
Hanford Atomic Products Operation
General Electric Company
3760 Building, 300 Area
Richland, Washington

HW/R-1533

Subject: PATENT REVIEW OF HW-SA-2663; CASE S-27,443

Dear Mr. Sharp:

Your letter of transmittal for the above case asked for patent clearance on report HW-SA-2663 on an urgent basis. We cannot give clearance for the paper with this material at the present time, ~~prior to September 1~~. Therefore, it would seem that deletions would be required. Since this is an analytical paper, we do not believe this would be too damaging to the paper. If we are able to get an early reply from the Central Office that allows such action, we will immediately give a full release.

Very truly yours,

George H. Lee

George H. Lee, Chief
Chicago Patent Group

UNITED STATES
ATOMIC ENERGY COMMISSION
CHICAGO OPERATIONS OFFICE
9800 SOUTH CASS AVENUE
ARGONNE, ILLINOIS

August 8, 1962

Mr. Robert Keith Sharp, Patent Attorney
Hanford Atomic Products Operation
General Electric Company
3760 Building, 300 Area
Richland, Washington

Subject: HWIR-1533 - AEC-S-27,443
HWIR-1534 - AEC-S-27,444

Dear Mr. Sharp:

We have assigned the above AEC case number(s) to the invention disclosure(s) which you recently sent to us. Please refer to the above number(s) in all future correspondence.

We will keep you informed as to the status of the above case(s).

Very truly yours,

Acting

George H. Lee, Chief
Chicago Patent Group

AEC-CH Form 236
(1-61)

August 3, 1962

H. J. Anderson
325 Bldg.
300 Area

R. J. Anicetti
325 Bldg.
300 Area

D. W. Brite
325 Bldg.
300 Area

Your Report of Invention entitled "A Method to Purify Nuclear Grade Uranium Dioxide (UO_2) Grain" has been designated HWIR-1533 and forwarded to the Chicago Patent Group of the Atomic Energy Commission for evaluation. It will then be sent by them to the Commission's patent counsel in Washington, D.C.

When the AEC has informed me of its intentions as regards the filing of an application in the U. S. Patent Office, the information will be communicated to you. In the meantime, please keep me informed as to significant developmental work done in connection with your invention or its actual or contemplated use beyond that described in your Invention Report. This may be done either by a written communication or a phone call to me.

As I understand it, hydrogen treatment to improve the O/U ratio had been used by others. If this is correct, the inclusion of water vapor becomes the basis for possible patentability. It would, therefore, be desirable to have experimental evidence of the improvement in purification brought about by the inclusion of water vapor. Also, some indication of the operative range of water concentration would be desirable.

Patent Attorney

RK Sharp:eg
3760 Bldg., 300 Area
Phone: 3601

cc: HWIR-1533
LB

Extension 3601 3760 Bldg., 300 Area

August 3, 1960

U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

Attention: Mr. George H. Lee, Chief
Chicago Patent Group

Gentlemen:

Enclosed herewith are three copies of an invention report, General Electric Case HWIR-1533, entitled "A Method to Purify Nuclear Grade Uranium Dioxide (UO_2) Grain", submitted by H. J. Anderson, R. J. Anicetti, and D. W. Brite.

The hydrogen treatment of UO_2 to adjust the O/U ratio has, I understand, been known previously[2]. The point of novelty in the present case is the use of the <u>moist</u> hydrogen. While the limits of water content have not been accurately determined as yet, the order of magnitude appears to be important. If the amount is too low, the impurities are not effectively removed. If it is too high, the O/U ratio is increased.

I understand that what I consider the invention originated by accident. It was observed that an improvement in results had occurred at a time when an assistant had allowed the dehydrating agent treating the hydrogen to become exhausted. The inventors hope to investigate the matter of water concentration in more detail.

References 1-4 are classified.

Two copies of HW-SA-2663 - Determination and Control of Nitrogen as Uranium Nitrides in Fused Uranium Dioxide (UO_2) are enclosed and clearance is requested for publication in ANALYTICAL CHEMISTRY. If clearance cannot be given promptly (by about September 1, 1962), we would appreciate being informed. The authors would then delete all passages disclosing the subject matter of this invention, thus limiting the paper to the determination of nitrogen.

While the invention is useful in connection with the PRTR, it apparently did not arise specifically under the Plutonium Recycle Program. I have not sent the disclosure to Mr. Robertson.

Very truly yours,

Robert Keith Sharp
Patent Attorney

RKS:eg

Enclosures

cc: USAEC-HOO - Att'n: Production Division

bcc: Record Copy
HWIR-1533
LB

54-3000-039 (9-56) AEC-GE RICHLAND, WASH.

HANFORD ATOMIC PRODUCTS OPERATION
GENERAL ELECTRIC COMPANY
RICHLAND, WASHINGTON

REPORT OF INVENTION

A.E.C. CASE NO.

G. E. CASE NO. HWIR-1533

TO: R. K. Sharp

I: ATTACHED HERETO IS A DESCRIPTION OF WHAT MAY BE AN INVENTION IN:

A method to purify nuclear grade uranium dioxide (UO_2) grain by heat treating of bulk supplies in a furnace, or a contained reaction vessel, for 4--66 hours at 800 °C - 1800°C in a (moist $\leq$ 1000 ppm water) hydrogen atmosphere. This method has been reduced to practice by a commercial vendor of UO_2 by following our instructions and specifications. Beneficial results were observed in purity, stoichiometry, density, and crystallinity. (See attached items)

II: THE NAME, TITLE OR POSITION, WORKS LOCATION, AND PERMANENT ADDRESS OF THE INVENTOR(S) IS:

H. J. Anderson, Engineer, HAPO., 819 W 23rd Place, Kennewick Washington
R. J. Anicetti, Specialist, HAPO., 613 Basswood, Richland, Washington
D. W. Brite, Engineer, HAPO., 403 Smith, Richland, Washington

III: EVIDENCE AS TO WHEN AND WHERE THE INVENTION WAS MADE CAN BE FOUND IN THE FOLLOWING LISTED WRITTEN OR PICTORIAL MATERIAL (NOTEBOOK, FILE REPORTS OR DRAWINGS, ETC.):

1) CFDO Monthly Report, October, 1961
2) HW-70557, Quarterly Report, April, May, June, 1961 page 5.15
3) HW-72346, Quarterly Report, October, November, December, 1961
4) HW-74377, Quarterly Report, April, May, June 1962
5) HW-SA-2663
6) Memo to E. A. Evans from R. J. Anicetti, May 7, 1962
7) Memo to E. A. Evans from H. J. Anderson, May 31, 1962

IV: THE APPROXIMATE DATE OF THE FIRST ENTRY IN SAID WRITTEN OR PICTORIAL MATERIAL DESCRIBING OR SHOWING SAID INVENTION IS:

October 1961

V: PERSONS WHO COULD TESTIFY AS TO WHEN AND WHERE THE INVENTION WAS MADE INCLUDE THE FOLLOWING:

W. E. Roake
D. R. de Halas

SIGNED (SUPERVISOR)	DATE	DEPARTMENT
E. A. Evans E A Evans	7-18-62	HLO - CFDO

NOTE: SUGGESTIONS FOR PREPARING THE INVENTION DESCRIPTION ARE CONTAINED ON THE REVERSE SIDE OF THIS FORM.

Received 7/26/62 Robert Keith Sharp
Patent Attorney

Report of Invention

Introduction

High density, uranium dioxide grain prepared by fusion or by electrodeposition from fused salt bath contains undesirable inclusions and impurities, such as, uranium metal, uranium carbides, uranium nitrides, and occluded salts. The amount of impurities included in the UO_2 often precludes its use as a nuclear fuel.

Ultra-high purity, dense UO_2 crystals are also required for basic studies of the properties both in- and ex-reactor. Large crystals, suitable for these studies are most conveniently obtained from UO_2 which has been fused in an electric arc furnace.

Invention

The chemical and physical properties of highdensity uranium dioxide grain were improved by our method of heat heating UO_2 grain in a furnace for time periods of 4 to 66 hours at 800 --1800 C temperature ranges in a (moist, ~1000 ppm water) hydrogen atmosphere.

Briefly, the method consists of the following procedure:

UO_2 **bulk material of various** sizes, but normally of -4 +20 mesh, is placed upon a tray with a suitable liner such as molybdenum, and inserted into a cool furnace. The furnace atmosphere is purged with an inert gas such as helium. Hydrogen gas containing moisture of at least 1000 ppm water is

Harlan J Anderson 7/18/62
Inventor Date

Robert J Anicetti 7-18-62 Daniel W. Bute 7-18-62
Inventor Date Inventor Date

Read and Understood by me this 7-18-62 ~~day~~ of 1962.

Witness Witness William E. Roake

admitted into the furnace. Excess hydrogen leaving the furnace is burned by a torch. The temperature is raised 100 - 200 C per hour to operating ranges of 800 - 1800 C but normally at 1750 C. The UO_2 grain remains at temperature for 4 - 66 hours, but normally for 16 hours duration. After turning off the furnace power, the UO_2 grain is cooled at 200 C per hour. When room temperature is attained, the UO_2 grain is removed from the tray and stored.

Both metallic and non-metallic impurities were removed by our method. The following tables, for examples, illustrate results of use of our method.

TABLE I

Ref. HW-70557, April - July, 1961

UO_2 (Fused) Grain

Item	Before	After	Remarks
O/U atomic ratio	1.96	2.00	4 hours at 1700 C
Gas Content CC/gm UO_2 (STP)	0.09	0.02	
Crystallinity	inclusions of 0.06 mm O.D.	voids of 0.008 mm O.D.	

TABLE II

Ref. HW-72346, October - December, 1961

UO_2 (Electrodeposited) Grain

Item	Before	After	Remarks
K	1400 ppm	360 ppm	10 hours at 1000 C
Pb	12,000 ppm	250 ppm	
Cl	1100 ppm	65 ppm	
O/U Atomic ratio	2.013	2.001	

Harley R. Anderson 7/18/62
Inventor Date

Robert J. Anicetti 7/18/62 David W. Brite 7-18-62
Inventor Date Inventor Date

Read and Understood by me this 7-18-62 day of 1962.

Witness Witness William E. Roake

TABLE III

Ref. HW-SA-2663, HW-74377, April - June, 1962

UO_2 (Fused) Grain

Item	Before	After	Remarks
N (as UN in UO_2)	1310 ppm	265 ppm	16 hours at 1750 C
N (as UN_2 in UO_2)	1220 ppm	230 ppm	

TABLE IV

Ref. HW-71422, July - September, 1961

UO_2 (High energy impact formed) Grain

Item	Before	After	Remarks
Density gm/cc	90-95% T.D.	99.5% T.D.	66 hours at 1800 C

Actual Use of Method

This method has been reduced to routine use in our laboratories for improving the purity, density, and crystallinity of UO_2 grain bulk supplies before use in fabrication of reactor fuel test elements. Large single crystals of UO_2 have been treated by this method to improve the chemical and physical properties of specimens useful in fundamental studies.

A commercial vendor has also reduced this method to practice by following our instructions and specifications for a production order of arc fused UO_2. After arc fusion of UO_2 grain, the material was immediately cooled in hydrogen rather than conventionally cooling the UO_2 in air or

Harlan J Anderson 7/18/62
Inventor Date

Robert J Anicetti 7/18/62 Daniel W. Brite 7-18-62
Inventor Date Inventor Date

Read and Understood by me this 7-18-62 day of 1962.

Witness _______________ Witness William E. Roake inert gas such as helium or argon. Chemical and physical properties of UO_2 were improved by our hydrogen atmosphere treatment method.

Interest in Method

Since this method improves the chemical - physical properties, and thereby enhances the integrity and composition of nuclear fuel materials, such as UO_2, that are currently used in pressed, swaged or vibrational compaction manufacturing processes for reactor fuel elements, we feel that important industrial interest is attached to our method. The method is of immediate interest to the USAEC fuels development and reactor programs, to the Hanford Plutonium Recycle Program, to commercial fuel processors such as NUMEC, Kerr-McGee, and Norton Companies, and to foreign countries and organizations such as U.K., Germany, Italy, France, Japan, and Euratom.

Attachments:

Harlan R. J. Anderson 7/18/62
Inventor Date

Robert J Anicetti 7/18/62 David W. Brite 7-18-62
Inventor Date Inventor Date

Read and Understood by me this 7-18-62 day, 1962.

Witness D. R. de Halas Witness William E. Roake

May 7, 1962

TO: E. A. EVANS

FROM: R. J. ANICETTI

FUSED UO_2 TREATMENT

During discussions with Norton Company personnel, I recommended a hydrogen atmosphere treatment immediately after arc-fusion to improve crystallinity, density, and stoichiometry. These tests were based upon our experiments conducted by H. J. Anderson, D. W. Brite and myself. Previously, fusions were cooled in air or argon.

cc: HJ Anderson
RJ Anicetti
letterbook

May 31, 1962

TO: E. A. Evans

FROM: H. J. ANDERSON HJA

Fused UO_2 Treatment

During discussions on May 28, 1962, with Norton Company personnel, especially Mr. N. Turnbull, I again asked about our tests fro hydrogen atmosphere treatment immediately after arc-fusion of UO_2 to improve crystallinity, density, stoichiometry and to remove impurities (metallic and non-metallic) such as uranium nitrides.

My understanding was that Norton Company would conduct the tests on Run 3 and tell us of the results.

cc: HJ Anderson
RJ Anicetti
letterbook

HW SA 2663
July 12, 1962

DETERMINATION AND CONTROL OF NITROGEN AS URANIUM NITRIDES IN FUSED URANIUM DIOXIDE (UO_2)

By Harlan J. Anderson and James C. Langford

Hanford Atomic Products Operation
General Electric Company
Richland, Washington*

Introduction

Reactor tests of UO_2 fuel elements can be abruptly terminated by cladding failures caused by excessive internal gas pressures. In our fuel fabrication development studies, therefore, an accurate analysis is required of fixed or sorbed gas content present in our fuel candidate materials before fabrication(1). Fused UO_2 is one of several candidate ceramic materials used in our studies.

Brite and Anderson have reported(3) on the presence, ease of formation, and possible mechanism of formation of uranium nitrides in fused UO_2. Anderson has also reported(4) that uranium mononitride (UN), uranium sesquinitride (U_2N_3), and uranium dinitride (UN_2) can act as copious nitrogen suppliers in fused UO_2.

In our laboratories, vacuum extraction and Kjeldahl techniques are used to analyze for fixed or sorbed gas content in UO_2 samples. Past efforts to correlate nitrogen values obtained by these two analytical techniques with calculated values of prepared samples containing known amounts of UN and UN_2 in UO_2 have not been successful. Nitrogen values for samples of commercial fused UO_2 supplies have also not been in agreement between vendor and our laboratories. Because of this inconsistency among analyses, study of these analytical techniques was under taken and completed.

A new analytical technique was developed and successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused UO_2.

---

* Work performed for the U. S. Atomic Energy Commission under Contract AT (45 1) 1350.

HW-SA-2663
July 12, 1962

Abstract

A new Kjeldahl digestion technique that uses a mixture of 1:1 diluted hydrochloric acid with additions of copper selenate and hydrofluosilicic acid was successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused uranium dioxide (UO_2). Generally used digestion techniques and vacuum extraction at 1000°C are inadequate for analysis of all uranium nitride species present in (fused) UO_2. An important adjunct to these studies showed that high nitrogen levels in UO_2 can be reduced to acceptable levels by heat treating bulk UO_2 supplies at 1750°C in moist hydrogen.

General Approach

Our observations and data showed that the bulk of the nitrogen present in fused UO_2 was present as fixed nitrogen in the form of uranium nitrides. The Kjeldahl technique, therefore, appeared the best approach for solution of our problem. Dissolution of UO_2 samples was considered of prime importance.

Reagents that might be effective in dissolving UO_2 have been reported (2). Determination of nitrogen in UO_2 has been reported(7) by Bennett using a method of oxidizing alkaline fusion followed by measurement of the volume of released nitrogen. Generally, the analytical approach for nitrogen determination was the Kjeldahl method with modifications of digestion techniques(8). A note(5) on a method for the determination of nitrogen content in uranium nitrides was important since these nitrogen species were identified as present in our fused UO_2 supplies.

The Kjeldahl approach was tried with an inclusive digestion technique for uranium nitrides in fused UO_2. Several digestion methods were tested using 100 milligrams (mg) samples of -100 mesh UO_2. Two prepared samples consisting of UN in UO_2 and UN_2 in UO_2 were used for each method.

Only nitrogen values obtained by digestion of the samples in a mixture consisting of 1:1 diluted HCl with additions of copper selenate and hydrofluosilicic acid were acceptable for both UN in UO_2 and UN_2 in UO_2 prepared samples.

Existing routine methods used in our laboratories gave poor results on both UN and UN_2 content in UO_2 prepared samples. One method consisted of sample digestion in concentrated HCl, or variations of diluted HCl with additions of zinc metal for generation of active hydrogen. Another method was a sample digestion in $HClO_4$ and H_2O_2 or Na_2O_2.

Apparatus and Reagents

Kjeldahl equipment, conventional laboratory glassware, and reagent grade chemicals were used unless otherwise stated.

A NaOH solution was made by dissolving 680 grams of NaOH in two liters of distilled water. Devarda's alloy, 0.5 grams, was added. Solutions were boiled until the volume was reduced to 1.8 liters(9). A mixed indicator of brom cresol green(6) and methyl red was used. Methyl red indicator was used to increase the sensitivity of the end point detection.

Procedure

Weigh out about 100 mg. of -100 mesh UO_2 sample into a 50 ml. beaker. Record actual weight. Then add 25 ml. of 1:1 HCl and 1 ml. of H_2SiF_6. Do not cover with a watch glass, but heat just below boiling for about 30 minutes. Add about 200 mg. of copper or potassium selenate. Digest until solution is complete.

Transfer the cooled sample solution to distillation Kjeldahl equipment and add 25 ml. NaOH solution. Start distillation to collect the condensate in a 50 ml. Erlenmeyer flask that contains the mixed indicator solution within the 5 ml. of 4% boric acid solution(6). Adjust the heat input so that 5 minutes after distillation begins, about 20 ml. of condensate will be collected. The boric acid solution need not be accurately measured(9).

Titrate the collected ammonia (ammonium borate) with a standard acid of 0.005 normality (N). Make a blank determination using the same amount of reagent as in the sample determination.

Calculate nitrogen content by the following formula:

$$\text{Parts per million (ppm) N (nitrogen)} = \frac{(\text{ml Titration} - \text{ml Blank}) \times N \times 14.007 \times 1000}{\text{Grams Sample}}$$

Duplicate results should agree within 0.3% relative.

Results and Discussion

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Generally used digestion techniques for Kjeldahl analysis, and vacuum extraction techniques for analysis of all uranium nitride species present in fused UO_2, were inadequate. A satisfactory technique was, however, developed and successfully used.

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Acknowledgement

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Literature Cited

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1. Hydrochloric Acid
2. Perchloric Acid and Hydrogen Peroxide
3. 1:1 HCl with additions of (copper) selenate and hydrofluosilicic acid.
4. Vacuum Extraction at 1000°C with mass spectrometric analysis of gases.

---

[a] Some U_2N_3 possible in sample

[b] New Digestion Technique

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		Nitrogen (ppm)	
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		Kjeldahl[a]	Vacuum Extraction 1000°C
UN (in UO_2)	1310	265	260
UN_2 (in UO_2)	1220	230	388

[a] New Digestion Technique

54-3000-101 (9-59)

DON'T SAY IT --- *Write It!*

DATE 3-29-63

TO Keith Sharp

FROM G. Jansen

I have investigated the references mentioned in the letter concerning the invention report HWIR-1533 [redacted]. These reports deal with the treatment of UO_2 in wet atmospheres to produce sintered and stoichiometric UO_2. No mention of other impurities than oxygen is made although the treatments described are nearly identical to those in the invention report. Recent telephone discussions with Wm. De Hollander with GE at San Jose have indicated that wet hydrogen at 1000°C has been successful in removing fluoride from relatively large UO_2 pellets, [redacted] with a probable application to chlorides also. The references investigated are listed on the reverse side of this sheet.

G Jansen

"TO MAKE LIFE LAST, PUT SAFETY FIRST"

① NP-6667 The Effects of Furnace Atmospheres on the Sintering behavior of UO_2, Webster, A.H. and N.F.H. Bright 2-5-58. Atmospheres: H_2, N_2+H_2, Ar, wet Ar, $Ar+O_2$, N_2, wet N_2, N_2+O_2, steam at 1200-1500°C. The effects of atmosphere and stoichiometry on UO_2 densification were studied.

② NP-8383 Sintering of Non-Stoichiometric UO_2 in different atmospheres Nordstrom, B. and U. Runfors. Studied O/U ratios and densities at 1100-15 in argon, H_2-H_2O atmospheres.

③ J. Amer. Ceramics Soc. 41:179-83(1958) C.A. Arenberg and P. Jahn varied furnace atmospheres, sintering aids, soaking time, furnace atmosphere

④ BRITISH PATENT 844980. Not listed in Chem. Abstracts. I have sent for a copy of the patent.

Extension 3601 3760 Bldg., 300 Area

August 3, 1962

U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

Attention: Mr. George H. Lee, Chief
Chicago Patent Group

Gentlemen:

Enclosed herewith are three copies of an invention report, General Electric Case HWIR-1533, entitled "A Method to Purify Nuclear Grade Uranium Dioxide (UO_2) Grain", submitted by H. J. Anderson, R. J. Anicetti, and D. W. Brite.

The hydrogen treatment of UO_2 to adjust the O/U ratio has, I understand, been known previously[2]. The point of novelty in the present case is the use of the moist hydrogen. While the limits of water content have not been accurately determined as yet, the order of magnitude appears to be important. If the amount is too low, the impurities are not effectively removed. If it is too high, the O/U ratio is increased.

I understand that what I consider the invention originated by accident. It was observed that an improvement in results had occurred at a time when an assistant had allowed the dehydrating agent treating the hydrogen to become exhausted. The inventors hope to investigate the matter of water concentration in more detail.

References 1-4 are classified.

Two copies of HW-SA-2663 - Determination and Control of Nitrogen as Uranium Nitrides in Fused Uranium Dioxide (UO_2) are enclosed and clearance is requested for publication in ANALYTICAL CHEMISTRY. If clearance cannot be given promptly (by about September 1, 1962), we would appreciate being informed. The authors would then delete all passages disclosing the subject matter of this invention, thus limiting the paper to the <u>determination</u> of nitrogen.

While the invention is useful in connection with the PRTR, it apparently did not arise specifically under the Plutonium Recycle Program. I have not sent the disclosure to Mr. Robertson.

Very truly yours,

Robert Keith Sharp
Patent Attorney

RKS:eg

Enclosures

cc: USAEC-HOO - Att'n: Production Division

bcc: Record Copy
HWIR-1533
LB

Awaiting Clearance – LB.

HW SA 2663
July 12, 1962

DETERMINATION AND CONTROL OF NITROGEN AS URANIUM NITRIDES IN FUSED URANIUM DIOXIDE (UO_2)

By Harlan J. Anderson and James C. Langford

Hanford Atomic Products Operation
General Electric Company
Richland, Washington*

Introduction

Reactor tests of UO_2 fuel elements can be abruptly terminated by cladding failures caused by excessive internal gas pressures. In our fuel fabrication development studies, therefore, an accurate analysis is required of fixed or sorbed gas content present in our fuel candidate materials before fabrication(1). Fused UO_2 is one of several candidate ceramic materials used in our studies.

Brite and Anderson have reported(3) on the presence, ease of formation, and possible mechanism of formation of uranium nitrides in fused UO_2. Anderson has also reported(4) that uranium mononitride (UN), uranium sesquinitride (U_2N_3), and uranium dinitride (UN_2) can act as copious nitrogen suppliers in fused UO_2.

In our laboratories, vacuum extraction and Kjeldahl techniques are used to analyze for fixed or sorbed gas content in UO_2 samples. Past efforts to correlate nitrogen values obtained by these two analytical techniques with calculated values of prepared samples containing known amounts of UN and UN_2 in UO_2 have not been successful. Nitrogen values for samples of commercial fused UO_2 supplies have also not been in agreement between vendor and our laboratories. Because of this inconsistency among analyses, study of these analytical techniques was under taken and completed.

A new analytical technique was developed and successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused UO_2.

---

* Work performed for the U. S. Atomic Energy Commission under Contract AT (45 1) 1350.

HW-SA-2663
July 12, 1962

Abstract

A new Kjeldahl digestion technique that uses a mixture of 1:1 diluted hydrochloric acid with additions of copper selenate and hydrofluosilicic acid was successfully used to analyze the nitrogen content (UN, U_2N_3, UN_2) in fused uranium dioxide (UO_2). Generally used digestion techniques and vacuum extraction at 1000°C are inadequate for analysis of all uranium nitride species present in (fused) UO_2. An important adjunct to these studies showed that high nitrogen levels in UO_2 can be reduced to acceptable levels by heat treating bulk UO_2 supplies at 1750°C in moist hydrogen.

General Approach

Our observations and data showed that the bulk of the nitrogen present in fused UO_2 was present as fixed nitrogen in the form of uranium nitrides. The Kjeldahl technique, therefore, appeared the best approach for solution of our problem. Dissolution of UO_2 samples was considered of prime importance.

Reagents that might be effective in dissolving UO_2 have been reported (2). Determination of nitrogen in UO_2 has been reported(7) by Bennett using a method of oxidizing alkaline fusion followed by measurement of the volume of released nitrogen. Generally, the analytical approach for nitrogen determination was the Kjeldahl method with modifications of digestion techniques(8). A note(5) on a method for the determination of nitrogen content in uranium nitrides was important since these nitrogen species were identified as present in our fused UO_2 supplies.

The Kjeldahl approach was tried with an inclusive digestion technique for uranium nitrides in fused UO_2. Several digestion methods were tested using 100 milligrams (mg) samples of -100 mesh UO_2. Two prepared samples consisting of UN in UO_2 and UN_2 in UO_2 were used for each method.

Only nitrogen values obtained by digestion of the samples in a mixture consisting of 1:1 diluted HCl with additions of copper selenate and hydrofluosilicic acid were acceptable for both UN in UO_2 and UN_2 in UO_2 prepared samples.

Existing routine methods used in our laboratories gave poor results on both UN and UN_2 content in UO_2 prepared samples. One method consisted of sample digestion in concentrated HCl, or variations of diluted HCl with additions of zinc metal for generation of active hydrogen. Another method was a sample digestion in $HClO_4$ and H_2O_2 or Na_2O_2.

Apparatus and Reagents

Kjeldahl equipment, conventional laboratory glassware, and reagent grade chemicals were used unless otherwise stated.

A NaOH solution was made by dissolving 680 grams of NaOH in two liters of distilled water. Devarda's alloy, 0.5 grams, was added. Solutions were boiled until the volume was reduced to 1.8 liters(9). A mixed indicator of brom cresol green(6) and methyl red was used. Methyl red indicator was used to increase the sensitivity of the end point detection.

Procedure

Weigh out about 100 mg. of -100 mesh UO_2 sample into a 50 ml. beaker. Record actual weight. Then add 25 ml. of 1:1 HCl and 1 ml. of H_2SiF_6. Do not cover with a watch glass, but heat just below boiling for about 30 minutes. Add about 200 mg. of copper or potassium selenate. Digest until solution is complete.

Transfer the cooled sample solution to distillation Kjeldahl equipment and add 25 ml. NaOH solution. Start distillation to collect the condensate in a 50 ml. Erlenmeyer flask that contains the mixed indicator solution within the 5 ml. of 4% boric acid solution(6). Adjust the heat input so that 5 minutes after distillation begins, about 20 ml. of condensate will be collected. The boric acid solution need not be accurately measured(9).

Titrate the collected ammonia (ammonium borate) with a standard acid of 0.005 normality (N). Make a blank determination using the same amount of reagent as in the sample determination.

Calculate nitrogen content by the following formula:

$$\text{Parts per million (ppm) N (nitrogen)} = \frac{(\text{ml Titration} - \text{ml Blank}) \times N \times 14.007 \times 1000}{\text{Grams Sample}}$$

Duplicate results should agree within 0.3% relative.

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The preliminary work as performed on two samples consisting of UN in UO_2 and UN_2 in UO_2. The results in Table 1 show that several digestion techniques are available or used for analyzing nitrogen as uranium nitrides in UO_2. Only the recommednded technique, however, gave complete recovery of the nitrogen. An important feature of this digestion technique is the action of the selenate ion. Lathouse et al(5) showed the selenate ion is essential to the digestion process.

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PATENT SPECIFICATION

NO DRAWINGS

844,980

THE PATENT OFFICE
LONDON

Date of Application and filing Complete Specification: March 18, 1958.
No. 8617/58.
Application made in United States of America on April 9, 1957.
Complete Specification Published August 17, 1960.

Index at Acceptance: Class 1(3), A1N36.
International Classification: C01g

Method of producing dense uranium oxide bodies.

COMPLETE SPECIFICATION

We, UNITED STATES ATOMIC ENERGY COMMISSION, 1901 Constitution Avenue, Washington, District of Columbia, United States of America, an agency of the United States Government established by the Atomic Energy Act of 1946 (Public Law 585) and the Atomic Energy Act of 1954 (Public Law 703), do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the production of dense uranium oxide bodies that are particularly suitable for use as fuel elements in atomic reactors or furnaces.

In the operation of such reactors considerable heat is generated from the fuel elements and is customarily dissipated by water cooling. At the elevated temperature involved, however, water vapor or steam has a strong tendency to corrode and disintegrate such fuel elements which must therefore be designed to withstand these effects. Inasmuch as porous bodies are more easily penetrated, and hence more subject to such deteriorating influences, high density, and consequently low porosity, is highly desirable from this standpoint. Accordingly, the minimum actual density of uranium oxide elements, as compared to the theoretical density of the material, should be about 90%, and a density ratio of 95% or higher is commonly specified.

A further factor in the design of atomic fuel elements is capacity to retain fission gases generated within the fuel elements during operation of the reactor. There is evidence to indicate that the capacity of a fuel element to retain such gases increases with its density, and extremely dense bodies are desirable for this reason as well.

Heretofore uranium oxide fuel elements have been molded in pellet form and such pellets densified by sintering in a hydrogen atmosphere at a temperature of about 1750° C. for a period of time up to 10 hours. This consumes a considerable amount of hydrogen, a relatively expensive material. Furthermore, the attainment of such temperatures generally requires special furnaces constructed with molybdenum or tungsten heating elements. Such furnaces are expensive to construct, and limited as to firing capacity. Also, they must be operated in a special non-reactive atmosphere such as hydrogen, helium, or argon to protect the heating elements. As a result the hydrogen firing operation, while quite effective for the purpose, is extremely expensive.

It is then a primary purpose of the present invention to meet the need for a more economical method of sintering uranium oxide bodies to a high density. It is a further purpose to provide such a sintering method capable of being carried out at lower temperatures, for example about 1300°C., attainable in a conventional type furnace, such as a muffle furnace with silicon carbide type resistance heating elements. Another purpose is to minimize the use of hydrogen and substitute a less expensive sintering atmosphere.

These ends may be achieved by practising our present invention which consists in a method of producing a dense uranium oxide body which comprises sintering in a steam atmosphere a body of uranium oxide grains having an oxygen-uranium atomic ratio not over 2.04, said grains having a particle size of less than 1 micron average diameter. Preferably said ratio is less than 2.02 and the sintering temperature is 1300°—1400°C.

Uranium oxide, in its reduced state, or lowest state of oxidation, theoretically contains oxygen and uranium atoms in a ratio of 2 to 1, as indicated by the formula UO_2. It readily takes up additional oxygen however, and commercially available material usually has a somewhat higher ratio.

(Price 3s. 6d.)

PROPER

Before such commercial material is molded and fired into fuel elements or other bodies, it is granulated to impart proper molding properties. In this operation the uranium oxide is mixed with liquids, binders, and lubricants to form a wetted mass suitable for conversion into granules having a range of particle sizes particularly suitable for molding a uniform body.

If the uranium oxide contains coarse grains or large aggregates, it is necessary to break these up so that the ultimate grains are smaller than one micron average diameter. It is customary to ballmill the uranium oxide to achieve this desired size reduction and/or deagglomeration; however, other physical or chemical methods which achieve the same result are equally suitable.

We have now found that, during the customary ballmilling operation, the ratio of oxygen to uranium atoms (hereafter referred to as O/U ratio) increases to a value of 2.10 to 2.20 depending on the length of time involved. We have further found that this change in the O/U ratio substantially interferes with sintering of this material in steam in accordance with the present invention, thus defeating the purposes of the invention. The manner in which the extra oxygen atoms are held is not definitely known. However powder X-ray diffraction analyses indicate that no new crystal structure is involved, but rather that a type of chemisorption occurs with the oxygen being held along crystallite boundaries and apparently producing fractures in, and consequent reduction in size of, the crystallites.

In any event, it is essential for present purposes that excess oxygen be removed so that the uranium oxide, prior to steam sintering, has an O/U ratio of 2.04 or less. While material with a ratio up to 2.04 can be sintered to a relatively dense body, optimum densities require a ratio under 2.02 and such lower ratio is preferred.

Reduction is conveniently accomplished by a hydrogen firing step prior to steam sintering. We have found that satisfactory results can be obtained by firing uranium oxide bodies in a hydrogen atmosphere for a period of about two hours at about 1200°C. just prior to the steam sintering step. At higher temperatures sintering is initiated to such an extent that the resulting crystallites do not respond in the desired manner to the steam sintering process.

The bodies may also be brought to a temperature of about 1200°C. in a hydrogen atmosphere, but this is unnecessary and uneconomical since equally good results can be obtained with other types of firing atmospheres in this initial heating period. While a steam atmosphere may be used in this initial heating, it is generally desirable to employ a neutral or reducing atmosphere such as nitrogen or cracked ammonia, providing such materials are readily available.

In a typical firing operation, shaped bodies are introduced into a cold furnace and a flow of gas, such as nitrogen, or steam, started in the furnace or firing muffle and maintained while the temperature is raised to about 1200°C. The furnace is held at that temperature for two hours with a flow of hydrogen replacing nitrogen. At the end of this time the hydrogen atmosphere is replaced with a steam atmosphere and the temperature raised to about 1300°C. and maintained at this temperature for about four hours.

While it is generally more convenient to perform the reduction just prior to steam sintering and then sinter in situ, this is not essential. Thus the reduction may even be performed prior to granulating and pressing or at any intermediate stage, providing the material is maintained at the desired low O/U ratio up to the time of steam sintering.

Surprisingly enough we have found that the O/U ratio increases during the course of such steam firing to about 2.19. In view of this circumstance it seems rather anomalous to reduce the ratio in the ballmilled material prior to steam sintering. However, repeated experiments have confirmed that such reduction is a prerequisite to effective steam sintering.

The actual sintering temperature required for a particular purpose will depend on the material density desired and will also vary with time of sintering. The following table indicates densities obtained with graduated sintering times and temperatures, and will serve as a guide in practising the invention.

Temperature in °C.	*Time in hrs.*	*Density in gm/cc*	*Density in %*
1200	8	10.39	94.8
1300	1	10.06	91.8
1300	2	10.32	94.2
1300	4	10.60	96.7
1400	1	10.48	95.6
1400	2	10.57	96.4
1500	1	10.60	96.7

PROPERTY OF U. S. GOVERNMENT

The data in the last column represent the percentage ratios of the actual densities in the preceding column to a theoretical density of 10.96 gm/cc.

Below 1200°C. sintering occurs so slowly, if at all, as to be negligible. Even the 8 hour time at 1200°C. is generally too long to be practical. On the other hand it is difficult to attain temperatures over 1400°C. without special firing furnaces involving heating elements sensitive to oxidation. For these reasons it is generally preferable to employ a sintering temperature of 1300-1400°C.

We have further found that the nature of the sintered material is dependent on the post-sintering or cooling treatment. If the sintered body is cooled in a steam atmosphere, X-ray diffraction tests indicate that the resulting mixed crystal structure is composed of two cubic phase crystals, UO_2 and $UO_{2.25}$, in the ratio of approximately 1:3. However, if the steam atmosphere is replaced at the completion of sintering and the sintered material cooled in a reducing atmosphere such as hydrogen, a single cubic phase crystal structure having the diffraction pattern of UO_2 and having an O/U ratio of 2.03 or less is obtained.

WHAT WE CLAIM IS:—

1. A method of producing a dense uranium oxide body which comprises sintering in a steam atmosphere a body of uranium oxide grains having an oxygen-uranium atomic ratio not over 2.04, said grains having a particle size of less than 1 micron average diameter.

2. The method set forth in claim 1 in which the oxygen-uranium atomic ratio is less than 2.02.

3. The method set forth in claim 1 in which the sintering temperature is 1300—1400°C.

4. The method set forth in claim 1 in which the body is fired at a temperature of 1200°C. for a period of about two hours in a hydrogen atmosphere to reduce the ratio of oxygen and uranium atoms to a value not greater than 2.04 prior to steam sintering.

5. The method set forth in claim 1 in which the uranium oxide from which the body is produced is initially subjected to a size reduction operation in which the oxygen-uranium ratio is increased and, prior to the sintering step, the ratio is reduced to a value not exceeding 2.04.

6. The method set forth in claim 1 in which the sintered product is cooled in a steam atmosphere.

7. The method set forth in claim 1 in which the sintered product is cooled in a hydrogen atmosphere.

8. The method of sintering a molded body of uranium oxide which comprises bringing the body to a temperature of at least 1200°C. with an oxygen-uranium ratio, on an atomic basis of not over 2.04, and introducing and maintaining a steam atmosphere over the body while it is held at the sintering temperature.

MARKS & CLERK

of London.

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Published at the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.