~~CONFIDENTIAL~~

UNCLASSIFIED

CF-56-8-128

METALLURGY AND CERAMICS (M-3679, 18th Ed.)

Do Not
STAT

UNITED STATES ATOMIC ENERGY COMMISSION

**THE APPLICATION OF LOW-ENRICHMENT
URANIUM DIOXIDE TO ALUMINUM
PLATE-TYPE FUEL ELEMENTS**

By
R. C. Waugh
J. E. Cunningham

August 2, 1956

Oak Ridge National Laboratory
Oak Ridge, Tennessee

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmission or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.

~~CONFIDENTIAL~~

Technical Information Service Extension, Oak Ridge, Tenn.

AEC RESEARCH AND DEVELOPMENT REPORT

UNCLASSIFIED

DECLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONFIDENTIAL

This report has been reviewed under the Declassification Guide of 1955.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission: makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe private rights; or

B. Assumes any liability with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Printed in USA. Charge 30 cents. Available from the Technical Information Service Extension, P. O. Box 1001, Oak Ridge, Tennessee. Please direct to the same address inquiries covering the procurement of classified AEC reports.

CONFIDENTIAL

AEC, Oak Ridge, Tenn.

1
UNCLASSIFIED

CF-56-8-128

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report; or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

**THE APPLICATION OF LOW-ENRICHMENT URANIUM DIOXIDE
TO ALUMINUM PLATE-TYPE FUEL ELEMENTS**

By

R. C. Waugh

J. E. Cunningham

Price \$ 0.30

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

August 20, 1956

CLASSIFICATION CANCELLED

DATE APR 1 1957

For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

Work performed under Contract No. W-7405-Eng-26

OAK RIDGE NATIONAL LABORATORY
Operated by
Union Carbide Nuclear Company
Post Office Box P
Oak Ridge, Tennessee

UNCLASSIFIED

~~CONFIDENTIAL~~

THE APPLICATION OF LOW-ENRICHMENT URANIUM DIOXIDE *
TO ALUMINUM PLATE-TYPE FUEL ELEMENTS

R. C. Waugh and J. E. Cunningham

Oak Ridge National Laboratory, Oak Ridge, Tennessee

INTRODUCTION

The Geneva Conference Display Reactor was designed by Oak Ridge National Laboratory upon the principles of a pool type reactor. Its fuel elements, however, contained uranium which was limited in U-235 enrichment to 20% because the reactor was for foreign use. This restriction had the effect of increasing the total uranium content per fuel element to an extent that would have necessitated use of a uranium-aluminum alloy containing 50 w/o uranium. Satisfactory casting and fabrication techniques for this alloy were not available at the time, and there were reservations about the success of a crash development effort. The severe limitation of having only three and one-half months to develop the necessary fabrication techniques and to complete fuel element manufacture, in addition to the increasing pressure of international publicity, made the decision critical. On the basis of limited, encouraging results then available, it was decided to use the $\text{UO}_2\text{-Al}$ system and thus fabricate the cores by powder metallurgy rather than by alloy techniques.

FUEL ELEMENT DESIGN

The fuel was incorporated into the fuel plates of the element in the form of 20% enriched UO_2 uniformly dispersed in an aluminum powder matrix. The basic design data are summarized in Table I.

FABRICATION PROCEDURE

The powder metallurgy components are minus 100 mesh aluminum powder which has been vacuum annealed for two hours at 600°C and enriched UO_2 powder in the minus 100 plus 325 mesh particle size

* Paper presented at Ames, Iowa, Metallurgical Information Meeting, May 2-4, 1956.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

range. After batch proportioning and blending, the amount of powder mixture required for each core compact is loaded into a die cavity and hydraulically pressed cold under a pressure of 33 tsi. The weighing and pressing operations are conducted inside separate dry boxes especially designed for handling enriched powder. A green core density of approximately 95% of theoretical is attained by pressing. A piece of 0.002 inch thick aluminum foil was pressed on the top and bottom surface of each core to assist in obtaining sound core-clad bonding. The resulting dispersion of the UO_2 particles in a pressed core is illustrated in Figure 1.

Each core is deliberately made 0.025 inches thicker than the frame. Prior to billet assembly, the core is inserted into the frame cavity and hydraulically pressed; thus the cavity is completely filled out. This operation eliminates blistering which may otherwise occur at the core-frame interface during subsequent fabrication. The assembled parts are held in place by tack welding. An exploded view illustrating the component parts which make up the assembled composite billet for rolling is shown in Figure 2.

The composite fuel plate is thoroughly heated at 590°C and hot rolled from the initial thickness to 0.070 inch, in order to achieve metallurgical bonding. The rolling schedule consists of six separate hot passes to yield a total reduction in thickness of 91 per cent. Excess stock is trimmed after flourescopically marking.

At this stage, the composite fuel plates are flux annealed to prevent the formation of objectionable blisters. The flux annealing treatment consists of coating the surfaces of the plates with a slurry mixture of alcohol and Eutectic 190 brazing flux and annealing for one hour at 600°C. After treatment, the water-soluble flux is removed by a scrub wash. The plates are then dipped in an acid bath of 15 HNO_3 - 1 HF - 84 vol % water solution, rinsed in hot water, and dried.

The composite fuel plates are reduced cold in several passes to final thickness of 0.060 $\pm$ 0.001 inch and stress annealed for one and one-half hours at 500°C. All acceptable plates are examined under a flourescopic x-ray screen to locate internal defects, determine straightness, and delineate the fuel bearing core section of the composite plate. After rough shearing, the fuel plates are stacked and batch machined to final width and thickness. The fuel plates are then annealed for one hour at 600°C. Prior to assembly, the composite fuel plates are curved to the desired 5.5 inch radius of curvature.

The curved fuel-bearing plates are joined into a single fuel assembly by brazing. Eighteen fuel plates are spaced at 0.117 inch apart and brazed into a pair of 1/8 inch thick side or spacer plates to form an integral fuel assembly or element.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

The grooved side plates of the fuel element are prepared from braze-clad sheet stock. This material is a duplex sheet consisting of wrought aluminum sheet, clad on one side only with 12% silicon-aluminum brazing alloy. After batch-machining the stock to final length and width, the grooves are cut through the braze-clad side of the plate by gang milling.

Prior to brazing, all component parts of the fuel element are thoroughly cleaned and handled thereafter with white cotton gloves. The side plates are coated with a slurry of alcohol and brazing flux and positioned upright in the drying jig. The fuel plates are inserted into the proper grooves, aligned, and tightened.

The assembled fuel component is then taken through the following sequence of operations which constitute the brazing cycle:

1. Dry in an oven at 150°C for three hours to drive off the alcohol and water from the hygroscopic brazing flux.
2. Transfer component from the drying oven to a ceramic brazing jig.
3. Heat for one hour at 450°C to thoroughly preheat the component and brazing jig.
4. Braze at 600°C in a forced air circulation furnace for thirty-five minutes.
5. Cool to room temperature and wash to remove the brazing flux.
6. Clean in an acid bath, and follow by hot water rinsing and drying.

Figure 3 illustrates a Geneva Conference type fuel element in place in the self-aligning, AlSiMag brazing jig.

FUEL ELEMENT MANUFACTURE

Experience obtained in the production of the Geneva Conference Display Reactor fuel elements clearly indicates that Al-UO₂ is a non-equilibrium system at the fabrication temperatures involved. A severe reaction may occur between the aluminum and the UO₂ during fabrication which manifests itself in dimensional growth and warpage of the fuel plates. Several plates which illustrate the deleterious effects of this reaction after final annealing of the plates are shown in Figure 4. Such growth would continue during the subsequent brazing operation and, since constrained, would result in a reject element due to out-of-tolerance plate spacings. The blistering shown in the upper two plates is the type which may be eliminated by improving the core-frame fit. Figure 5 shown the core of a plate which illustrates the reaction. The complete consumption of the smaller oxide particles, as well as the

~~CONFIDENTIAL~~

646 004

~~CONFIDENTIAL~~

peripheral attack of the larger particles, is to be noted. The primary reaction products have been identified by x-ray diffraction, chemical dissolution, and spectrographic techniques as being UAl_3 , UAl_4 , and Al_2O_3 . A section of the core of a plate in which no reaction between the $Al-UO_2$ has yet occurred is shown in Figure 6.

Initial development work was with depleted peroxide precipitated UO_2 which had been laboratory high fired at $2000^\circ C$ in a hydrogen atmosphere. This oxide was found to be relatively non-reactive with aluminum during the fabrication procedure.

Fuel element production was initiated using enriched oxide which had been high fired at an equipment-limitation-imposed maximum temperature of $1750^\circ C$. Oxide produced by the steam oxidation of uranium chips and peroxide precipitation were found to react to a large degree during fabrication. A total of nearly five hundred cores and plates were lost during this initial effort. A variety of processing modifications failed to solve the problem.

Preliminary investigation revealed that oxide prepared by a new method, then at an intermediate stage of laboratory development, was relatively non-reactive with aluminum during fabrication.⁽¹⁾ The basic steps in the preparation of this material, baptized at the time as "Genevieve Oxide," are as follows:

UO_3 monohydrate crystals are grown hydrothermally in an autoclave at $250^\circ C$ for ten hours from a UO_3 hydrate, (peroxide cake)-10 per cent uranyl nitrate-aqueous solution. The UO_3 hydrate crystals are reduced and sintered by high firing in hydrogen at $1750^\circ C$. The resultant UO_2 has the same external shape as its parent but is about two-thirds its size.

UO_3 monohydrate, anhydrous UO_3 , and UO_2 crystals are shown in Figure 7. The UO_2 is the larger black fraction. The smaller fraction is composed of UO_3 monohydrate and anhydrous UO_3 crystals.

Experiments performed with oxide prepared by this new method were so encouraging that it was decided to scale-up for production of the enriched oxide from 400 gm laboratory lots to six kg production batches. Indeed, in light of the critical time schedule, there was no alternative. Unfortunately, however, process control was lost during scale-up. The quality of the oxide produced varied almost from run to run, and it was noted that at no time during the sustained production was the quality of the UO_2 crystal attained equivalent to that which had been characteristic of the initial, limited development work.

The reactivity of the UO_2 with aluminum appears to be a function of the surface to volume ratio of the oxide particles. Thin platelets, rods, agglomerates, particles containing adherent surface fines due to excessive grinding, and fines themselves were found to accelerate reaction.

~~CONFIDENTIAL~~

CONFIDENTIAL

C46 005

~~CONFIDENTIAL~~

Chunky oxide particles in the minus 100 plus 325 mesh size range were generally acceptable. It is estimated that nearly forty per cent of the total oxide produced by the reduction of UO_3 hydrate was unsatisfactory for use and had to be recycled.

The criteria for continued reaction was time at temperature. Studies on plates containing highly reactive UO_2 revealed that growth continued through all of the high-temperature fabrication operations. Accelerated growth rates were observed at the higher temperature operations, during which plate dimensions were found to increase as much as two per cent.

The majority of the elements brazed had plate spacings within $\pm 15\%$ of nominal, which was the revised specification. In twenty-eight per cent of the elements brazed, the plate spacing variation exceeded $\pm 30\%$.

An overall view of a completed fuel element with attached accessories is shown in Figure 8. A transverse view of a fuel element showing the fuel plate curvature and the Al- UO_2 core section is shown in Figure 9.

The primary reaction products have been identified as UAl_3 , UAl_4 , and Al_2O_3 .⁽²⁾ Reaction rate curves are characterized by an apparent "incubation period" during which the reaction initially progresses very slowly, followed by a period during which the reaction occurs very rapidly, and then by a final period in which the reaction rate decreases progressively. The duration of the incubation period appears to be determined by the oxide used.

It is possible that a major portion of the fuel plate growth, which has accompanied reaction, may be due to hydrogen which has been adsorbed by the UO_2 lattice during the reduction and high firing operations.⁽³⁾ As the UO_2 lattice is consumed during reaction, the hydrogen released into the matrix could cause growth. Mass spectrographic analyses of the gases liberated from several compacts during reaction have shown them to contain approximately 96% hydrogen.

IRRADIATION RESULTS

The first radiation damage information on aluminum fuel plates containing 54 w/o UO_2 in an aluminum matrix was obtained from the irradiation of full-size elements in the Low Intensity Test Reactor at Oak Ridge and in the Materials Testing Reactor at Arco. Both of these elements contained UO_2 which had been prepared by the reduction of UO_3 monohydrate and were similar in design to the Geneva reactor element.

The testing conditions for each element are shown in Table II. Neither element showed any evidence of distortion from radiation damage. Several plate spacings were measured at random locations on the MTR

046 006
~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

element and were ascertained to be experimentally equivalent to the corresponding pre-irradiation measurements.

SUMMARY

Although considerable trouble was encountered, a loading of fuel elements for the Geneva Conference Display Reactor was successfully made, using 20% enriched UO_2 in a matrix of aluminum. Proper selection and control of the UO_2 should retard the Al-UO_2 reaction sufficiently to permit economical fuel element manufacture. Preliminary irradiation results on full-size fuel elements of this type are encouraging.

ACKNOWLEDGMENT

The contributions of the following members of the Oak Ridge National Laboratory to this paper are gratefully acknowledged: J. H. Erwin and J. H. Coobs developed and administered fuel element manufacture; M. L. Picklesimer, J. H. Frye, Jr., J. L. Gregg, E. J. Boyle, and W. O. Harms guided the study of the Al-UO_2 reaction; H. A. Davis performed gas analyses; R. M. Steele and H. L. Yakel, Jr. performed x-ray diffraction analyses; J. R. Johnson and A. J. Taylor developed the method for producing the UO_2 which was used in the GCR elements and also conducted the UO_2 quality control program; R. J. Beaver coordinated the irradiation testing program; and R. J. Gray did much of the metallography study.

~~CONFIDENTIAL~~

646 007

DECLASSIFIED

CONFIDENTIAL

Table I

Summary of Basic Design Data for GCR Fuel Elements

Number of fuel bearing plates-----	18
Water gap spacing, mil-----	117
Total plate thickness, inches-----	0.060
Clad-core-clad thickness, mil-----	17.5 - 25 - 17.5
Width and length of active core, inches-----	2.5 x 23-5/8
Core mixture composition, wt %-----	54 UO ₂ - 46 Al
UO ₂ particle size, microns-----	44 - 149
U-235 distribution per plate, gm/cm ² -----	0.025
U-235 enrichment factor, %-----	20 nominal
U-235 content per assembly, gm-----	170
Metal to water volume ratio-----	0.63

Table II

Test Conditions for Two Geneva Conference Reactor
Fuel Elements

<u>Reactor</u>	<u>Time in Reactor (days)</u>	<u>Irradiation (Mwd)</u>	<u>Flux (neutrons cm⁻² sec⁻¹)</u>	<u>Estimated Burnup of U-235, %</u>
LITR	83	209	1.5×10^{13}	5
MTR	36	964	2.5×10^{14}	23

CONFIDENTIAL

~~CONFIDENTIAL~~

~~-9-~~

Figure 1 (Y-17403)

100X

Dispersion of UO_2 Particles in Pressed Core

DECLASSIFIED

046 009

~~CONFIDENTIAL~~

-10-

Exploded View Showing Makeup of Composite Fuel Plate Prior to Rolling.

Figure 2 (Y-15937)

Exploded View Showing Makeup of Composite Fuel
Plate Prior to Rolling

046 010

03712291030

CONFIDENTIAL

-11-

Figure 3 (Y-15939)

GCR Type Fuel Element in Place in Brazing Jig

046 011

DECLASSIFIED

~~CONFIDENTIAL~~

-12-

Figure 4 (Y-15056)

Fuel Plate Warpage and Blistering

046 012

037028030

~~CONFIDENTIAL~~

-13-

Figure 5 (Y-16828)

200X

Al-UO₂ Reaction in Core of Fuel Plate

046 013

DECLASSIFIED

CONFIDENTIAL

-14-

Figure 6 (Y-16829)

200X

Fuel Plate Core Showing No Al-UO₂ Reaction

046 014

0371229.030

~~CONFIDENTIAL~~

-15-

Figure 7 (24426)

Approx. 15X

UO₃ Monohydrate, Anhydrous UO₃ and UO₂ Crystals

DECLASSIFIED

046

015

~~CONFIDENTIAL~~

-16-

Figure 8 (Y-16733)

Completed GCR Fuel Element with Attached Accessories

046 016

03712091030

~~CONFIDENTIAL~~

~~17~~

Figure 9 (Y-15938)

Transverse Section of Completed GCR Fuel Element

046 017

DECLASSIFIED

1-18

~~CONFIDENTIAL~~

References

	Page
1. J. R. Johnson, L. M. Doney, S. D. Fulkerson, A. J. Taylor, J. M. Warde, G. D. White, "The Technology of Uranium Dioxide, A Reactor Material," ORNL-2011.....	5
2. M. L. Picklesimer (Unpublished Work).....	6
3. L. E. J. Roberts, "The Adsorption and Absorption of Gases by Uranium Dioxide," A.E.R.E. C/R 887.....	6

~~CONFIDENTIAL~~

046 018

0077291030

CONFIDENTIAL

CONFIDENTIAL

037128.030