MASTER

GA-2881

PREPARATION OF $(\text{Th}, \text{U})\text{C}_2$ FUEL PARTICLES FOR THE HTGR

By
Walter V. Goeddel
Howard E. Shoemaker

November 12, 1962

General Atomic Division
General Dynamics Corporation
San Diego, California

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.

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, expressed 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, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

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

Printed in USA. Price \$0.50. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

GENERAL ATOMIC

DIVISION OF

GENERAL DYNAMICS

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

P.O. BOX 608. SAN DIEGO 12. CALIFORNIA

GA-2881

METALS, CERAMICS, AND MATERIALS

PREPARATION OF $(\text{Th}, \text{U})\text{C}_2$ FUEL PARTICLES FOR THE HTGR

Work done by:

W. V. Goeddel
P. R. Macy
G. Norman
J. M. Pontelandolfo
H. E. Shoemaker
J. H. Thompson

Report written by:

Walter V. Goeddel
Howard E. Shoemaker

ABSTRACT

A process that has been developed for the preparation of particles of thorium-uranium dicarbide is described. Granulated particles composed of powdered UO_2 , ThO_2 , and carbon are suspended in a bed of graphite flour and heated to convert the oxides to dicarbides. The particles are then melted to densify and spheroidize them, the graphite flour keeping them separated so that they will not flow together.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONTENTS

ABSTRACT	i
I. INTRODUCTION	1
II. LITERATURE REVIEW	2
III. PREPARATION OF (Th, U)C ₂ PARTICLES	4
Graphite-Bed Sintering and Melting Process for (Th, U)C ₂ Particles	4
Materials	8
Composition	8
Particle Agglomeration	9
Sintering (Reacting) and Melting	9
Particle Separation and Sizing	9
REFERENCES	12
Appendix--GENERAL ATOMIC REPORTS DEALING WITH COATED- PARTICLE FUELS AND GRAPHITE-MATRIX FUEL COMPACTS.	14

I. INTRODUCTION.

The fuel (U^{235}) and fertile material (Th^{232}) for the Peach Bottom High-temperature Gas-cooled Reactor (HTGR) are in the form of carbides uniformly dispersed as particles in a portion of the graphite moderator. The $(Th, U)C_2$ particles are from 100 μ to 400 μ in diameter. Each particle is pyrolytically coated with a 50- to 60- μ thickness of dense carbon to protect the fuel material from oxidation reactions during fuel fabrication and to increase the retention time of fission products during reactor operation.

A review of research on pyrolytic-carbon-coated carbide fuel particles and graphite-matrix fuel compacts for the Peach Bottom HTGR has been presented in a recent publication. ⁽¹⁾ The present report describes the process developed for the preparation of the $(Th, U)C_2$ particles.

A bibliography of General Atomic reports dealing with coated-particle fuels and graphite-matrix fuel compacts, which originally appeared in Ref. 1, is reproduced in the Appendix.

II. LITERATURE REVIEW

Rounded particles of lead and other metallic materials have for many years been made by pouring from the top of shot towers. Molten metal is fed through a perforated pan, and surface tension causes the particles to assume a spherical shape during the free fall. To avoid flattening, the shot is allowed to drop into water. In 1936, Vogt was issued a patent on a similar process in which glass spheres were made by dropping pieces of glass through a hot zone and a subsequent cooling zone. (2)

During the past few years, a number of people have investigated ways of preparing spherical particles of refractory metals, carbides and oxides, including nuclear fuel materials. Crouthamel and coworkers prepared high-density spherical ThO_2 particles of 1- to 50- μ diameter with up to 10 atom-% UO_2 . (3) Small particles produced by spraying a sol spheroidized and were gelled with an ammonia-air mixture during free fall after spraying. Subsequent sintering produced dense oxide particles. Williams was able to produce UO_2 spheroids by crushing cold compacting UO_2 powder, spheroidizing these particles by gyration on an abrading surface, and subsequently sintering. (4) He made dense UO_2 particles of 100- to 350- μ diameter. Other investigators have been able to make spherical particles of metals and carbides by such processes as dropping through a hot zone (shot tower), (5) centrifugal melting, (6) and powder metallurgical processes. (7)

The very high temperatures of plasmas have recently been applied to the melting and spheroidizing of refractory particles. Browning prepared B_4C spherical powders with a plasma jet, (8) Thorpe reports the preparation of UO_2 spherical powders, (9)(10) and Sturge and Smyth (11) discuss the preparation of ZrO_2 , UC_2 , and ThC_2 spheroids, also by plasma-jet techniques. Murray also spheroidized refractory materials with a plasma jet. (12)

Among the disadvantages of the plasma-jet processes are high flame velocities and contamination of the product by vaporization of the electrodes. In a series of recent publications, Reed (13, 14, 15) and Hedger and Hall (16)(17) discuss the use of the induction-coupled plasma torch for the preparation of spherical powders. This device affords a source of very high-temperature and low-velocity gases that are free of electrode contamination. Uranium compounds are among the materials reported to have been spheroidized with the plasma torch. However, the size of the particles produced by both the plasma-jet and plasma-torch devices has generally been limited to less than 50 μ by the short residence time of the irregularly shaped feed particles within the high-temperature plasma.

A high-intensity, three-phase arc furnace has been used by Benesovsky and Rudy to prepare (Th,U)C₂ spherical particles.⁽¹⁸⁾ Sintered (Th,U)C₂ is ground, and the particles are dropped through the three-phase arc, where they melt and spheroidize, and then through a cooling zone, where they solidify. This is very similar to the process patented by Vogt in 1936,⁽²⁾ but a much higher-temperature heat source is used in the present device.

All of the above-described techniques for producing dense, spherical particles by melting require suspension or free fall of the particle during the time it is molten. In 1962, a different process was described by Cathro and Walkley.⁽¹⁹⁾ They were able to prepare small spheres of metals such as gold, silver, and lead by dispersing pieces in a refractory matrix powder in order to isolate the particles during melting. For example, small pieces of gold were suspended in MgO powder, heated above the melting point, and subsequently cooled and separated from the MgO powder. This process had been developed independently at General Atomic for the preparation of (Th,U)C₂ particles.

III. PREPARATION OF (Th, U)C₂ PARTICLES

Several techniques were investigated for producing rounded (Th,U)C₂ particles of 200- to 400- μ diameter from the metal oxides and carbon. These techniques fell into two general classifications: (1) the materials were reacted and then formed into particles, and (2) the materials were formed into particles and then reacted. Several examples of each type of process received experimental evaluation.

ThO₂ and UO₂ powders were chosen for starting materials to minimize costs. For each type of process the metal oxide powders were agglomerated with carbon powder, and the aim was to produce the carbide particles in molten form to encourage high density and sphericity.

One process in particular appeared quite promising. The agglomerated pellets of mixed ThO₂, UO₂, and carbon powders were suspended in fine graphite powder in a graphite container and heated in vacuo to 2100° to 2300°C to convert the oxides to dicarbides. The temperature was then raised above the melting point of the carbides (~2450°C) to densify and spheroidize the particles. The powdered-graphite bed prevented the particles from flowing or sintering together, and in fact a partial graphite coating adhered to the surface of the particles. The excess graphite powder was readily separated from the carbide particles by screening.

Particles prepared by this "graphite-bed sintering and melting" process were found to be of high density, and X-ray diffraction showed them to be (Th, U)C₂. Starting with granulated particles 300 to 420 μ in diameter, carbide particle yields of 80% 175 to 250 μ and 95% 175 to 300 μ were obtained. Since this appeared to be the most promising process for early fruition, it was selected for Peach Bottom HTGR particle fabrication. Particles prepared by this technique are shown in Figs. 1 through 6.

A brief description of the graphite-bed sintering and melting process for the preparation of (Th, U)C₂ particles is presented below.

GRAPHITE-BED SINTERING AND MELTING PROCESS FOR (Th, U)C₂ PARTICLES

Powdered ThO₂, UO₂, and carbon are mixed and formed into particles about 75 μ larger than the carbide particles desired. These particles

(75x)

Fig. 1--Photomicrograph of (Th, U)C₂ particles produced by sintering and melting in a powdered graphite bed

(210x)

Fig. 2--Photomicrograph of (Th, U)C₂ particle produced by sintering and melting in a powdered graphite bed

(575x)

Fig. 3--Photomicrograph of portion of $(\text{Th}, \text{U})\text{C}_2$ particle produced by sintering and melting in a powdered graphite bed; note graphite inclusions and coating

(1000x)

Fig. 4--Photomicrograph of portion of $(\text{Th}, \text{U})\text{C}_2$ particle produced by sintering and melting in a powdered graphite bed; note adhering coating of graphite

(250x)

Fig. 5--Photomicrograph of UC_2 particle produced by sintering and melting in a powdered graphite bed

(75x)

Fig. 6--Photomicrograph of UC_2 particles produced by sintering and melting in a powdered graphite bed

are dispersed in graphite powder and heated to over 2000°C in vacuo to cause reduction of the oxides to the mixed dicarbide. The temperature is then raised above the melting point of the $\text{ThC}_2\text{--UC}_2$ to cause densification. The graphite powder prevents the molten particles from sticking together.

Since excess carbon is present in the bed during sintering (reaction) and melting, it has been found desirable to prepare the eutectic mixture, $(\text{Th, U})\text{C}_2\text{--C}$, rather than the stoichiometric dicarbide. This also makes melting the particle easier.

MATERIALS

The optimum materials for particle preparation by this process were found to be as follows:

ThO_2	nuclear grade, fine particle size
UO_2	nuclear grade, fine particle size
Carbon	Pettinos 6353, fine particle size
Binder	ethyl cellulose
Vehicle	trichloroethylene

Other carbons (GP-38, Speer 170), binders (methyl cellulose, pitches, resins, polyvinyl alcohol, shellac, Lucite, bakelite, furfuryl alcohol resin, paraffin, etc.), and vehicles (water, benzene) may also be used.

Composition

Sufficient carbon is required to reduce the oxides to dicarbides and, in most cases, form the eutectic mixture. Two per cent binder is optimum. Compositions to produce some various carbide particles are given below:

1. UC_2	85.0 g UO_2 15.1 g carbon powder
2. ThC_2	85.0 g ThO_2 15.5 g carbon powder
3. $\text{ThC}_2\text{--UC}_2$ (Th:U = 10:1)	80.0 g ThO_2 8.0 g UO_2 16.0 g carbon powder
4. $\text{ThC}_2\text{--UC}_2\text{--C}$ eutectic (Th:U = 10:1)	70.0 g ThO_2 7.0 g UO_2 16.7 g carbon powder

Number 4 is the Peach Bottom composition.

Particle Agglomeration

The powdered ThO_2 , UO_2 , carbon, and ethyl cellulose are mixed together dry; then the trichloroethylene is added to dissolve the binder and form a slurry. Continued mixing produces agglomerated particles (granulating process). Large batches are most readily prepared in a P-K Twin-Shell Blender with intensifier bar; small batches and reworking of off-size particles are done in a Hobart mixer. Particles from mixers are oven-dried at 140°F and then sieved to obtain 295- to $495\text{-}\mu$ (+48 -32 mesh) particles. Off-sized particles are recycled through the mixing operations with the addition of more trichloroethylene.

Sintering (Reacting) and Melting

The presized, agglomerated particles are mixed with graphite flour in an 8-to-1 particle-to-graphite ratio by weight, and loaded into a graphite crucible. The loaded crucible is placed in the heating apparatus (Figs. 7,8, 9), evacuated, and heated to 2000° to 2200°C to reduce the oxides to dicarbides. A marked decrease in outgassing signals the completion of the reaction process, and the temperature is then raised to about 2500°C to melt and densify the particles.

Particle Separation and Sizing

After cooling, the crucible is transferred to an inert-atmosphere glove box and the contents (graphite powder and $(\text{Th}, \text{U})\text{C}_2$ particles) are sieved using 35- and 100-mesh screens. The material in the pan is graphite powder insulation and a very small percentage of undersized particles. This mixture is reused directly as insulation in subsequent runs. Yields of 150- to $420\text{-}\mu$ particles should be about 99%. Particles are stored in sealed containers until coated with pyrolytic carbon.

Fig. 7--Graphite-bed sintering and melting apparatus for the preparation of $(\text{Th}, \text{U})\text{C}_2$ particles

Fig. 8--Graphite crucible and quartz chamber used for the preparation of $(\text{Th, U})\text{C}_2$ particles

Fig. 9--The quartz container is heated to about 900°C while the particles are being melted at 2500°C

REFERENCES

1. Goeddel, W. V., Pyrolytic-carbon-coated Carbide Fuel Particles and Their Use in Graphite-matrix Fuel Compacts, General Atomic Report GA-3588, October 30, 1962. This report was presented at the meeting on Ceramic Coated Particle Nuclear Fuels, November 5-6, 1962, at Battelle Memorial Institute, Columbus, Ohio, and will be printed in the Proceedings of that meeting.
2. Vogt, U.S. Patent 2,038,251 (1936).
3. Crouthamel, C., W. Knapp, S. Skladzien, and J. Loeding, Preparation of High-density, Spherical Thorium Oxide Particles with up to 10 Atom Per Cent Uranium, Argonne National Laboratory Report ANL-6340, June, 1961.
4. Williams, N., A Method for the Production of Dense Uranium Dioxide Spheroids, Metallurgy Division, U.K.A.E.A. Research Group, Atomic Energy Research Establishment, Harwell, Report AERE-M-888, July, 1961.
5. Wahll, M. J., J. R. Van Orsdel, and R. B. Fischer, "Spheroidization of Irregularly Shaped Metal Powders," Powder Met., No. 8, p. 48 (1961).
6. Himmelstein, P., B. Liebmann, and L. Schafer, 4th Plansee Seminar, Reutte/Tyrol, 1961.
7. Gorlé, F., J. Van Geel, and E. Jonkheere, 4th Plansee Seminar, Reutte/Tyrol, 1961.
8. Browning, J. A., "Plasma--A Substitute for the Oxy-Fuel Flame," Welding J., (N.Y.), September, 1959.
9. Thorpe, M. L., "The Plasma Jet and Uses," Research and Development 11, 1 (1960).
10. Thorpe, M. L., "Plasma Jet--Progress Report 2," Research and Development, p. 77, (June, 1961).
11. Sturge, D., and R. Smyth, Forming of Refractory Spheroids by Plasma Jet and the Development of a Plasma Furnace, Dragon Project Report No. 56, October, 1961.
12. Murray, P., 4th Plansee Seminar, Reutte/Tyrol, 1961.

13. Reed, T. B., The Induction-Coupled Plasma Torch, MIT Lincoln Laboratories Report 83G-0096, September, 1960.
14. Reed, T. B., "Induction-Coupled Plasma Torch," J. Appl. Phys. 32, 821 (1961).
15. Reed, T. B., "Plasma Torches," International Science and Technology, p. 42, (June, 1962).
16. Hedger, H. J., and A. R. Hall, Preliminary Observations on the Use of the Induction Coupled Plasma Torch for the Preparation of Spherical Powder, Metallurgy Division, A. E. R. E., Harwell, August 10, 1961.
17. Hedger, H. J., and A. R. Hall, "Preliminary Observations on the Use of the Induction-Coupled Plasma Torch for the Preparation of Spherical Powder," Powder Met., No. 8, p. 65, (1961).
18. Benesovsky, F., and E. Rudy, Development of the Fabrication Processes of Fission Product Retaining Fuels, Metallwerk Plansee, CON/WIN/51081.
19. Cathro, K. J., and A. Walkley, "The Preparation of Small Metal Spheres," J. Sci. Instrum. 39, 312 (1962).

Appendix

GENERAL ATOMIC REPORTS DEALING WITH COATED-PARTICLE FUELS AND GRAPHITE-MATRIX FUEL COMPACTS

1. GA-1235, 40-Mw(e) Prototype High-temperature Gas-cooled Reactor Research and Development Program, Quarterly Progress Report for the Period Ending December 31, 1959.
2. GA-1378, ibid., Quarterly Progress Report for the Period Ending March 31, 1960.
3. GA-1640, ibid., Quarterly Progress Report for the Period Ending June 30, 1960.
4. GA-1774, ibid., Quarterly Progress Report for the Period Ending September 30, 1960.
5. GA-1982, ibid., Quarterly Progress Report for the Period Ending December 31, 1960.
6. GA-2204, ibid., Quarterly Progress Report for the Period Ending March 31, 1961.
7. GA-2493, ibid., Quarterly Progress Report for the Period Ending June 30, 1961.
8. GA-2747, ibid., Quarterly Progress Report for the Period Ending September 30, 1961.
9. GA-2861, ibid., Quarterly Progress Report for the Period Ending December 31, 1961.
10. Anderson, E. E., P. E. Gethard, and L. R. Zumwalt, Recent Data Obtained on Fission Products Released from (Th, U)C₂-Particle-Graphite Fuels, GA-3119, May, 1962.
11. Anderson, E. E., P. E. Gethard, and L. R. Zumwalt, Steady-state Release Fraction of Krypton and Xenon Fission Products at High Temperatures from (U, Th)C₂-Graphite Fuel Matrix in Out-of-Pile Experiments, GA-3211, June, 1962.
12. Engle, G. B., Metallography of Carbide Fuel Compounds, GA-2067, March, 1961.
13. Engle, G. B., Development of Carbon-coating Process for (Th, U)C₂ Fuel Particles, GA-2301, October, 1961.

14. Engle, G. B., C. S. Luby, and J. C. Bokros, Evaluation of (Th, U)C₂, Carbon-coated (Th, U)C₂ Particles, and Carbon Coatings, GA-3067, April, 1962.
15. Goeddel, W. V., The Development and Evaluation of Graphite-matrix Fuel Compacts for the HTGR, GA-2289, August, 1961.
16. Goeddel, W. V., G. R. Tully, Jr., and R. A. Meyer, The Use of Graphite in High-temperature Nuclear Fuel Elements, GA-2304, September, 1961.
17. Goeddel, W. V., Summary of Coated-particle-fuels Development at General Atomic for the Period October, 1961, to April, 1962, GA-3109, April, 1962.
18. Goeddel, W. V. (ed.), Pyrolytic-carbon-coated Carbide Fuel Particles and Their Use in Graphite-matrix Fuel Compacts, GA-3588, October, 1962.
19. Goeddel, W. V., Coated Particle Fuels Development at General Atomic for the Period May-October, 1962, GA-3620, October, 1962.
20. Goeddel, W. V., Procedures for the Preparation of Graphite-matrix Fuel Compacts Containing Pyrolytic Carbon Coated (Th, U)C₂ Fuel Particles, GAMD-2221, April, 1961.
21. Goeddel, W. V., Thermal Stability Testing of Graphite-matrix Fuel Compacts Containing Pyrolytic-carbon Coated Carbide Particles with Comments on the Amoeba Effect, GAMD-2675, September, 1961.
22. Goeddel, W. V., Coated Fuels Irradiation Tests, A Materials Summary, GAMD-2729, October, 1961.
23. Goeddel, W. V. (ed.), Coated Fuel Particle Newsletter, Part 1, GAMD-2646, April-June, 1961.
24. Ibid., Part 2, July, 1961.
25. Ibid., Part 3, August-September, 1961.
26. Ibid., Part 4, October, 1961.
27. Ibid., Part 5, November, 1961.
28. Ibid., Part 6, October-December, 1961.
29. Ibid., Part 7, January, 1962.
30. Ibid., Part 8, February, 1962.
31. Ibid., Part 9, May-July, 1962.
32. Luby, C. S., Apparatus and Procedure for Coating Thorium-Uranium Carbides with Carbon at 1000° to 1400°C, GA-2241, May, 1961.
33. A Review of Fuel Element Research and Development for the High-temperature Helium Gas-cooled Reactors, GA-2283, June, 1961.