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O.E.C.D. HIGH TEMPERATURE REACTOR PROJECT

DRAGON

Dragon Project Report

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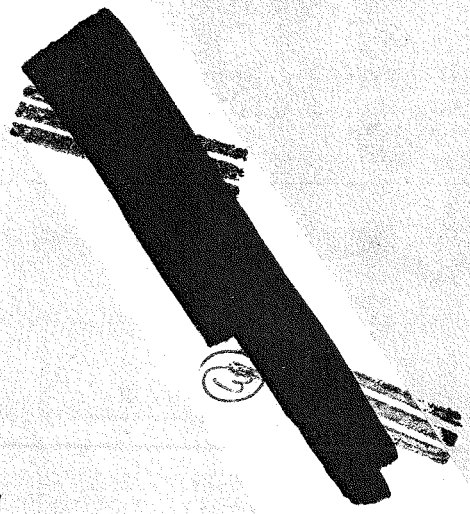
FABRICATION OF SPHEROIDIZED PARTICLES BY THE POWDER METALLURGY AGGLOMERATION PROCESS

by

F. GORLE, E. JONCKHEERE and J. VANGEEL
C.E.N. Mol.



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This report covers work which is performed under contract and any enquiries on the subject of this report should be addressed to the Chief Executive, O.E.C.D. High Temperature Reactor Project, (Dragon) A.E.E. Winfrith, Dorchester, Dorset, England.

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FABRICATION OF SPHEROIDIZED PARTICLES

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1. INTRODUCTION

During the year 1961 preliminary contacts took place between the DRAGON Project and the Department of Metallurgy of the C.E.N., and towards the end of the same year DRAGON made an official proposal for C.E.N. to work on spheroidized particles.

In a study conducted within the scope of the Euratom-United States Joint Research and Development Programme, and in collaboration with Belgo Nucléaire, the C.E.N. had developed a process for fabricating spherical particles of UO_2. [1] The Dragon Project required that a study be undertaken with the view to extend the above process to the fabrication of spherical particles of thorium and uranium carbides.

The official contract began one year ago, in January, 1962. During the course of the year numerous exchanges of personnel and ideas took place. Consequently, personnel connected with the Dragon Project visited Mol on several occasions to follow the progress of the contract and become acquainted with the techniques employed. Likewise engineers of the C.E.N. went often to Winfrith, to discuss the process and to facilitate its development in glove-boxes.

2. DESCRIPTION OF THE PROCESS PREVIOUSLY EMPLOYED

A large effort has been devoted during the past few years to the production of spheroidized UO_2 and UC particles for use in dispersion type fuel elements. The object was to develop a process which could eventually be applied to plutonium compounds, and therefore requiring a high total efficiency. The spherical particles were fabricated according to the following technique:

The UO_2 powder had the following characteristics:

(a) produced by decomposition of A.D.U.

(b) surface: 4.5 to 6 m^2/g

(c) tap density: 2 to 2.22 g/cm^3

(d) O/U ratio: 2.07 to 2.13

(e) density: 2.56 in Hg and 9.57 in He.

The procedure was as follows:

- the UO_2 was mixed with 2.5 w/o (weight %) camphor in methyl alcohol, followed by
- ball milling for 15 minutes, and

- evaporation of the methyl alcohol at 100°C, under argon, for 15h

- the agglomerate was then sieved for 20 minutes (since the sieving apparatus involved a rotary action, the particles were simultaneously spheroidized)

- the particles in the appropriate size range were sintered.

The yield of particles of suitable size was approximately 30% per cycle. The remainder was easily recirculated at the ball milling stage. Tests were also carried out with a view to producing spherical particles by tumbling the agglomerates in a rotating cylinder, or in a container undergoing a planetary motion. These processes were suitable for powders having only one constituent, but the yield per pass was relatively low.

3. APPLICATION OF THE PROCESS TO URANIUM DICARBIDE, AND RESULTS

Considering the difference in the size range of the initial powder, it could be expected that the process described in 2. would not be directly applicable. The dicarbide obtained by reaction between the oxide and carbon, was ground to a size less than 40 microns. After mixing with a solution of camphor in isopropyl alcohol, it was placed in a planetary sieve and sized to the appropriate value. After sizing, the particles were placed in a rotating cylinder for spheroidization. The speed and time of rotation were regulated to produce particles of good quality (see Fig. 1 and 2).

It was thus shown that the process could be applied to particles of uranium dicarbide, or other materials.

The Dragon Project then decided to extend application of the process. The selection of the fuel has to be made ultimately according to the major criteria of irradiation resistance and fission product diffusion. Consequently the Dragon Project had to investigate several parallel paths to decide the eventual fabrication of specimens for irradiation. The major variables to be studied were as follows:

- should the particles be sintered or melted

- should the uranium particles contain a diluant to increase their irradiation resistance

- for fabrication of particles of the mixture $(Th,U)C_2$, should the starting material be thorium carbide (very active and not easily handled), or thorium plus carbon.

The C.E.N. was charged with investigating the fabrication of particles which could finally be used as such without subsequent fusion (and therefore with a controlled porosity).

The choice of diluant fell upon zirconium, which led to a study of the fabrication of particles starting from Zr + UC + C and ZrC + UC. Since working with thorium carbide is very delicate, the C.E.N. chose to fabricate the particles starting from the metal, and to carburise as late as possible in the sequence of fabrication.

4. FABRICATION OF MIXED Zr-U CARBIDE PARTICLES

Some tests were conducted starting from mixtures of Zr + C + UC, but since hafnium-free zirconium carbide is commercially available, it was decided to use mixtures of zirconium and uranium carbides. In addition, since the final goal was the production of complete fuel elements at Winfrith, a part of the effort was concentrated on the possibility of simplifying the fabrication techniques to enable an extrapolation to pilot plant scale production. Several different processes were studied with the view to simplifying the production of (Zr,U)C. One, fairly complicated method resulted in obtaining spheroidised particles of good dimensions and with a yield of the order of 50%, and is described below:

- the powders ZrC + UC, of diameter less than 18 microns, are mixed dry: then, after addition of 1 w/o camphor dissolved in methyl-isobutylketone, the mixture is compressed (at 4 T/cm^2) into pellets of about 90 g

- the pellets are crushed, then ground in a ball-mill (using TiC balls)

- the powder so obtained is added to 2 w/o camphor dissolved in the same solvent (ketone) and is placed on the upper tray of a planetary sieve, of mesh 480 microns; the grains are collected on the intermediate sieve of 350 microns where they are spheroidized.

This process, although giving a yield of 30% in 20 minutes of spheroidizing, had to be simplified. The successive stages are described below:

(a) The compressing operation, necessitating 3 stages, i.e. binder addition - compressing - crushing, had to be eliminated.

(b) To try to increase the yield and make the batches more uniform, it was attempted to control the evaporation of the solvent more precisely. To achieve this during the sieving operation, solvent is placed in the lower tray of the sieve assembly; this results, at a given temperature, in a constant partial pressure of the solvent vapour during the operations, preventing all evaporation from the mixture and allowing reproducible work on the powders without the preliminary compression.

Thus the method of production has now developed to the following:

- UC and ZrC powders are mixed dry in a V-mixer; camphor dissolved in methyl-isobutylketone is then added

- the product is immediately placed in the upper tray of a planetary sieve (the order of the sieves being: 350μ - 177μ - collecting tray).

After rotating for 1 hour the particles are recovered on the sieve of 177μ; the yield of suitably sized particles (250μ - 350μ) varies from 40% when a new sieve is put into use, to 65 - 70% in normal operation.

It is also possible to add the solvent and binder to the upper sieve and then to add the dry ZrC - UC mixture. This latter procedure has the advantage that the ZrC - UC mixtures can be prepared in large quantities and stored.

The process described here above has been tested for various UC and ZrC ratios (6/1, 8/1 and 15/1) and in fact the whole range of composition from UC to ZrC has been covered.

After spheroidization, the particles are sintered for 2 to 3h at 2000°C in vacuo. No sticking has been observed. Analysis of the particles after sintering (ratio 8/1) gives:

- structure: essentially ZrC. Parameter = 4.72 Å (ZrC - 4.696 Å, and UC - 4.955 Å)

- density in toluene: 7.55 to 7.68, i.e. 89 - 90.5% T.D.

The homogeneity has also been investigated: For instance, the U and Zr content has been measured in small batches and the results are shown in Table 1.

TABLE 1

Batch	U w/o	Zr w/o
37.4 mg	24.66	67.15
37.6 mg	25.85	65.90
39 mg	25.13	66.15

Particles are shown in Fig. 3 and 4.

5. COATING OF THE PARTICLES

Some tests for the fabrication of particles containing the carbides of both thorium and uranium have been conducted, starting from Th + UC_2 + C and the first laboratory results are satisfactory. Although its manipulation is done in glove boxes under inert atmosphere (see Fig. 5) the thorium carbide hydrolyses rapidly. So, the Dragon Project decided to lend us a fluidising furnace to enable the particles to be coated with a layer of pyrolytic carbon before being sent to England.

The first parts of the furnace arrived at the end of July, 1962, and the furnace was commissioned for the first time at the beginning of September, by Mr. H. Beutler of the Dragon Project. A leak in the main body (of brass) immobilised it for one month. Since October, tests on coating uranium dicarbide have been conducted. At the moment modifications to the furnace are being studied to enable the sintering to be effected in the fluidising unit.

The coating tests have been mainly conducted according to data supplied by Dragon, and specified principally by R.A.E. (Farnborough). (Mr. B. Bickerdike and his co-workers.)

The procedure is as follows:

The furnace is degassed at 10^{-3} mm Hg, then filled with Argon and the heating commenced; a preliminary layer of pyrolytic C is deposited by the cracking of propane at 1300°C, and a second layer by the cracking of methane at 1800°C. The UC_2 is generally coated according to the conditions given in the Table 2.

TABLE 2

Test No.	First layer				Second layer			
	Time min	Propane flow cc/min	Argon flow cc/min	Temp. °C read at the outer face of heating element	Time min	Methane flow cc/min	Argon flow cc/min	Temp. °C read at the outer face of heating element
5	20	368	1400	1270	60	420	1400	1800
6	20	368	1400	1260	60	420	1400	1790
7	20	368	1400	1255	30	420	1400	1800

Measurement of the thickness of the layer has given the results shown in Table 3 below:

TABLE 3

Test No.	Thickness in μ	Particle size in μ	Weight gain (g/g)
1	58	251	-
2	46.5	250	0.26
3	17.5	265	-
4	-	-	1.04

Fig. 6 shows UC particles coated 20 min at 1255°C and 30 min at 1800°C.

6. FUEL BASED ON THE OXIDE

Several facts have led us to believe that thorium oxide containing UO_2 could be envisaged as a fuel constituent for the Dragon Reactor:

(a) the great reactivity of the dicarbide

(b) the high reaction temperature of ThO_2 + C

(c) the difficulty of carburising uranium oxide, and thorium oxide, in an argon atmosphere.

The first attempts at coating were conducted on pure uranium oxide. It would be expected that the partial pressure of CO existing at the UO_2-C interface would limit the reaction by the diffusion of CO through the pyrolytic carbon.

The advantages of such a fuel are evident if the diffusion of the CO is sufficiently low:

(a) a cheap product after fewer stages of fabrication

(b) less reactivity of the product and hence permitting fabrication in a simplified dry box.

Compatibility tests will be carried out in this direction. Furthermore, preliminary tests have shown that it is very easy to fabricate particles of ThO_2-UO_2 of good quality.

In the case of the reaction ThO_2-C being too rapid, an intermediate layer (oxide, metal, nitride, carbide etc.,) could be envisaged.

7. CONCLUSIONS

(1) The process of fabrication of particles of ZrC-UC has been developed to the stage of production on the scale of 100 g, and is relatively simple.

Fig. 7 shows UO_2 particles sintered at 1750°C and coated: 20 minutes at 1250°C with propane and 60 minutes at 1790°C with methane.

(2) It is possible to fabricate particles of $(Th,U)C_2$ starting from $(Th + UC_2 + C)$, and tests to perfect the method are in progress.

(3) The unit for coating with pyrolytic carbon, lent by Dragon, is operating.

(4) A fuel based on thorium/uranium oxide (in place of carbide) is considered. The preliminary attempts to fabricate particles are favourable. Further investigation is in progress.

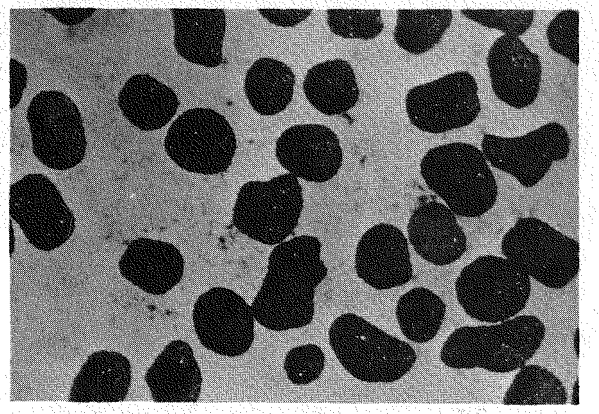
8. ACKNOWLEDGMENTS

We gratefully thank the Dragon Project for authorisation to publish these results. We thank especially Messrs R. Huddle and C. Vivante for fruitful discussions.

We also thank Mr. Driesen for the most valuable technical assistance given during the investigation.

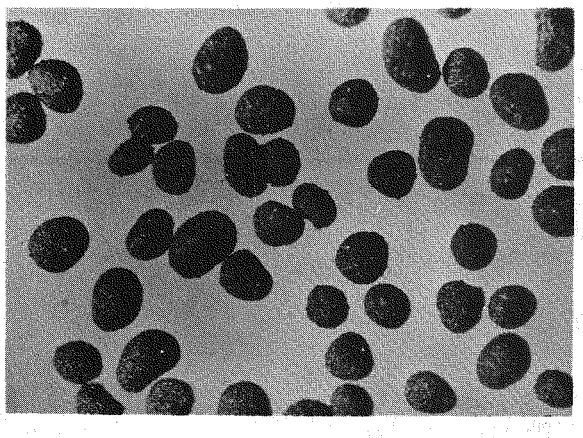
9. REFERENCES

[1] "Fabrication de particules sphériques" by F. Gorlé, J. Vangeel and E. Jonckheere. Discussion presented at the "Plansee Seminar: Pulvermetallurgie in der Atomkernteknik" June 20-24, 1961, Reutte.



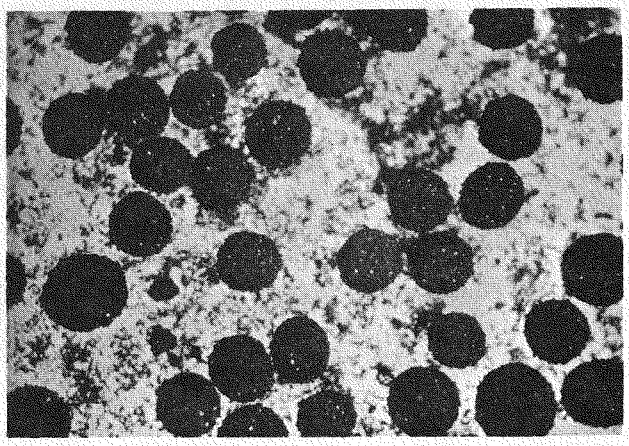
20 X

Fig. 1: (Zr,U)C Particles, after 10 Minutes Spheroidization



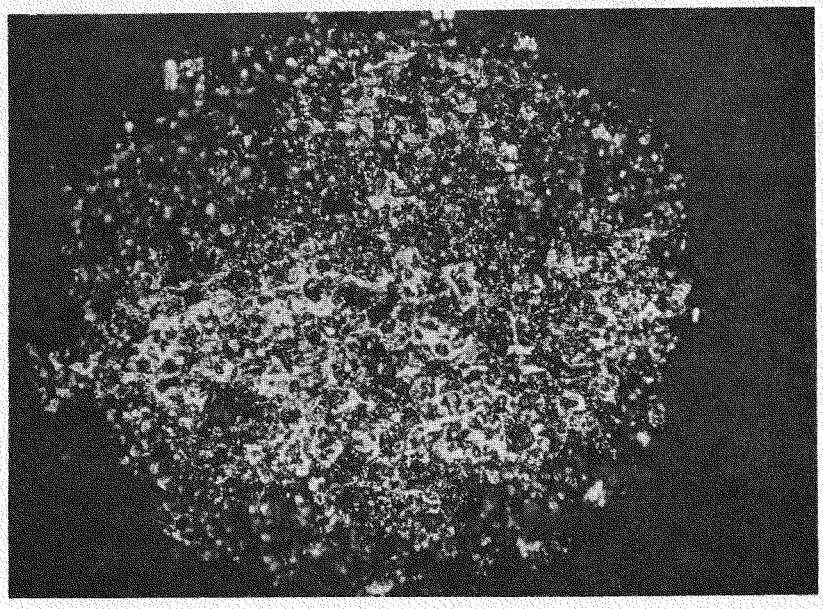
20 X

Fig. 2: (Zr,U)C Particles, after 1 Hour Spheroidization



20 X

Fig. 3: (Zr,U)C Particles, Fabricated following the New Process. ($\frac{Zr}{U}$ = 8/1)



300 X

Fig. 4: (Zr,U)C Particles, same Process, but after Sintering $2\frac{1}{2}$ Hours at 2000°C

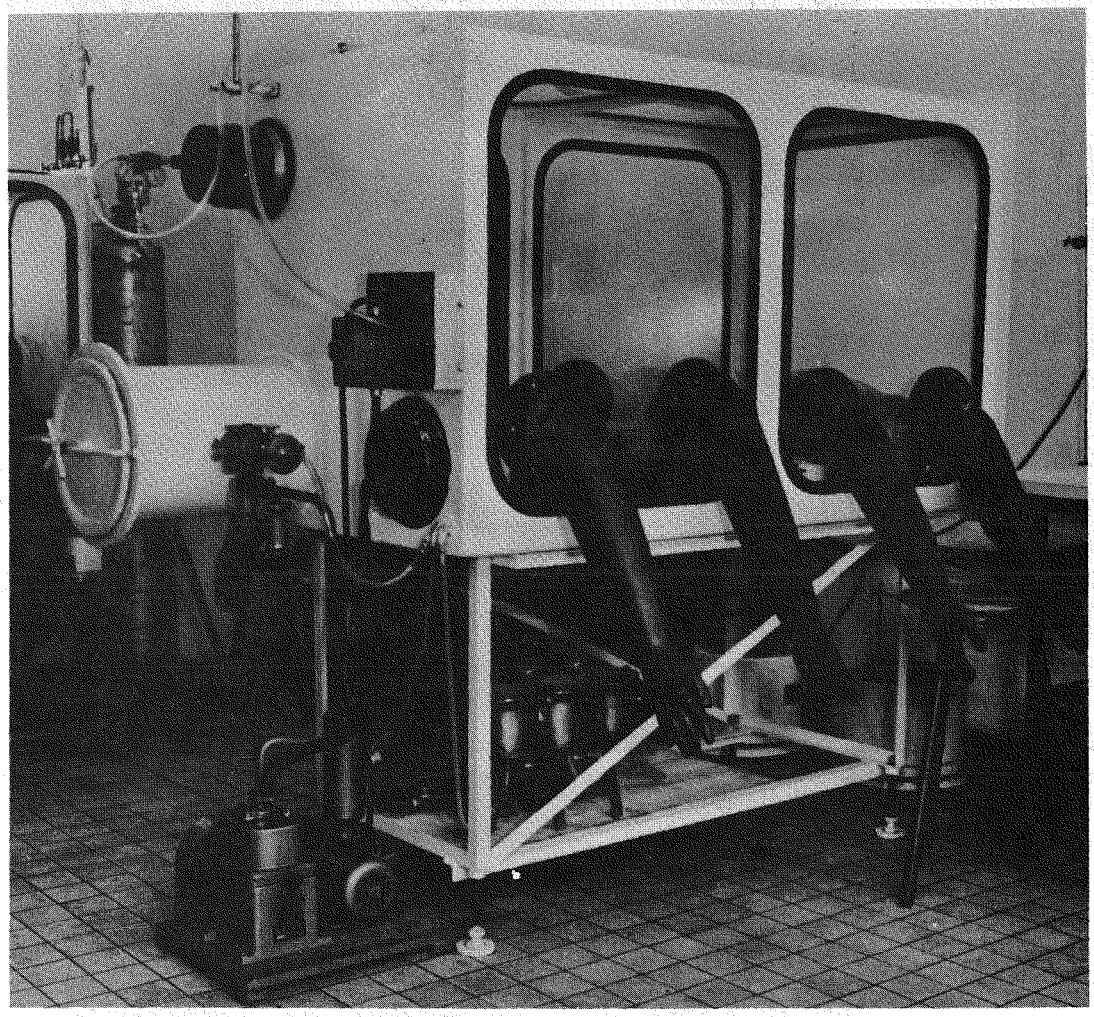
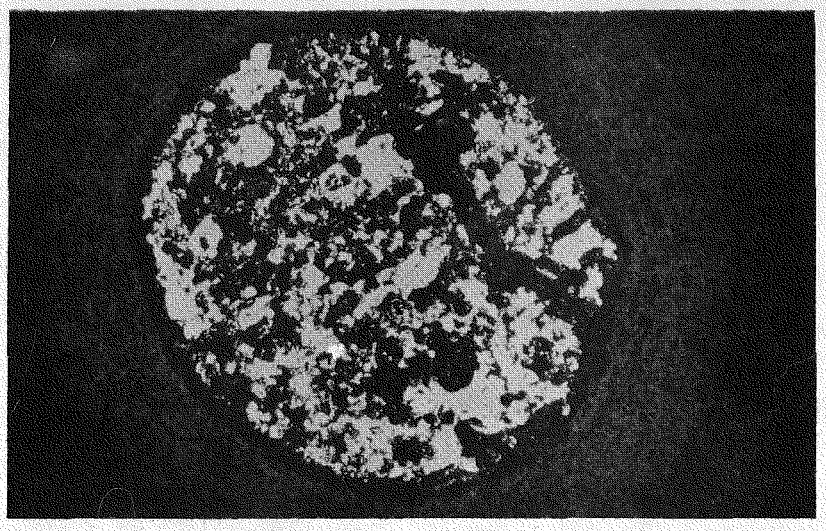
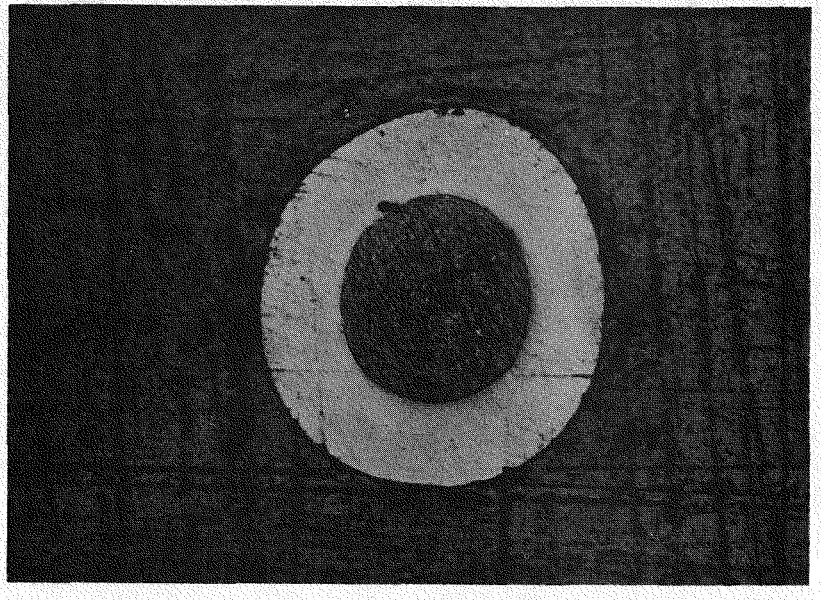


Fig. 5: Glove Box for the Manipulation of Carbide Particles



300 X

Fig. 6: UC Particles Coated 20 Minutes at 1255°C and 30 Minutes at 1800°C



200 X

Fig. 7: UO_2 Particles Sintered at 1750°C and Coated
(a) 20 Minutes at 1250°C with Propane
(b) 60 Minutes at 1790°C with Methane