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MASTER

Improved Graphite Matrix for Coated-Particle Fuel

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IMPROVED GRAPHITE MATRIX FOR COATED-PARTICLE FUEL

by

Donald H. Schell and Keith V. Davidson

ABSTRACT

An experimental process was developed to incorporate coated fuel particles in an extruded graphite matrix. This structure, containing 41 vol% particles, had a high matrix density, >1.6 g/cm³, and a matrix conductivity three to four times that of a pitch-injected fuel rod at 1775 K. Experiments were conducted to determine the uniformity of particle loadings in extrusions. Irradiation specimens were supplied for five tests in the High-Fluence Isotope Reactor at the Oak Ridge National Laboratory.

INTRODUCTION

High-Temperature Gas-Cooled Reactor (HTGR) fuel elements consist of hexagonal prismatic graphite blocks containing numerous longitudinal cylindrical holes. Some of the holes are used for helium cooling passages and others contain fuel sticks. The fuel sticks, ~13 mm in diameter, consist of ~50-mm-long segments made by a molding process. A tube is filled with a mixture of spherical particles consisting of a specified amount of coated fissile particles and coated fertile particles. Carbon shim particles are used to fill the remaining segment volume. This stack of particles is infiltrated with pitch or a mixture of pitch and a fine graphite flour. The fuel stick segments then are heat treated and eventually are placed in a hole in the graphite fuel element or are placed in the fuel element and heat treated in place. The main objection to this type of fuel stick is that the matrix carbon holding the spherical particles together has low density and thus poor thermal conductivity. Also, shim particles are required to complete the stack of particles to be infiltrated. The number of shim particles varies according to the number of fissile and fertile particles required in the fuel stick segment because the uranium and thorium loading will vary considerably in different locations in the reactor.

A program was started at the Los Alamos Scientific Laboratory (LASL) in 1973 to develop a fuel rod having high-temperature capabilities for possible use in a gas-cooled nuclear process heat reactor. There were two parts to the program, one to develop improved coated fuel particles that would increase the temperature capability of the fuel and the other to incorporate these particles in a dense graphite matrix using an extrusion process.[1]

An extruded fuel stick would be made as long as required in one piece, ~75 cm, and would not require any unloaded spherical shim particles. Each stick would have only the fissile and fertile particles required to obtain the desired loadings, contained in a high-density graphite matrix.

For the extrusion program, a nominal loading of 41 vol% particles was selected. This loading was held constant throughout most of the program to simplify the evaluation of experimental variables.

The extrusions contained 6 vol% fissile-size particles (~550-μm diam) and 35 vol% fertile-size particles (~800-μm diam), the approximate average content of an HTGR fuel stick.

EXPERIMENTAL PROCEDURE

Extrusions made early in the program contained spherical glass beads. These beads were used until spherical carbon particles and coated particles became available. The extrusions were very useful in working out extrusion mix composition, investigating various graphite filler flours, and measuring relative matrix densities. Information as to suitable die design, extrusion pressures, and relative extrusion strengths was also obtained. A partially polymerized furfuryl alcohol, Varcum 8251,* used extensively in making extruded graphitic fuels and shapes for the Rover (Nuclear Propulsion Reactor) program,[2] was used as the binder for practically all spherical-particle-loaded extrusions. Varcum is a thermosetting resin having a carbon residue, upon heat treatment, of 45 wt%. A thermosetting resin is desirable because it greatly simplifies the heat treatment of the extrusion while maintaining dimensional stability.

Numerous extrusions loaded with glass beads were made using several reactor-grade graphite flours. The glass beads approximated the sizes of the coated fissile and fertile particles mentioned previously.

The following flours were used.

*Reichhold Chemicals, Inc., Varcum Division.

	Description	Source
KX-88	−200 mesh equiaxed particles with relatively high CTE.[a]	Airco, Inc., Airco Speer Carbon-Graphite Div.
M3	−60 mesh equiaxed particles, medium CTE[a]	Great Lakes Carbon Corp.
S97	−200 mesh from stock similar to M3. The finer grind produced more acicular particles	Airco, Inc., Airco Speer Carbon-Graphite Div.
1074	−200 mesh, similar to S97	Great Lakes Carbon Corp.
GP-48	−200 mesh, graphite produced from a needle coke	Union Carbide Corp., Carbon Products Div.
9553	−200 mesh, low CTE[a]	Airco, Inc., Airco Speer Carbon-Graphite Div.
Thermax	Carbon black having spherical particles ~0.3-μm diam	R. T. Vanderbilt Company, Inc.

[a]Coefficient of thermal expansion.

A normal graphite extrusion would contain 85 parts of graphite flour to 15 parts of Thermax. The extrusions containing glass beads were made with and without Thermax and in one case with varying amounts of Thermax. The extrusions could be heat treated only to 925 K to insure that the glass beads would not melt. By burning a known volume of an extrusion and recovering the beads it contained, we could calculate the volume fraction of beads and the matrix carbon density. The matrix carbon density is defined as the density of the matrix in the volume it occupies; that is, the volume not occupied by the beads.

Data on these early extrusions are shown in Table I.

At best, all surfaces had a pebbly appearance caused by beads directly under the surface. There always seemed to be a carbon layer between the bead and the extrusion surface, however. Many surfaces had a badly crazed appearance and the extrusions were weak. These were mostly extrusions made with the finer graphite flours and especially those containing Thermax. This result was unexpected and can possibly be explained by the fact that during heat treatment, even to 925 K, the matrix shrinks, but is restrained by the relatively large beads, and thus cracking occurs.

The coarser M3 flour gave relatively good results both in the manner in which it extruded and in the quality of the product. Further extrusion experiments used this flour almost exclusively. It was the only coarse reactor-grade flour available at the time. Unloaded matrix extrusions were irradiated in the High-Fluence Isotope Reactor (HFIR) experiment HT-28.[3]

The impressions we obtained during this early development work did not change throughout the program.

A number of different fissile and fertile particles were incorporated in the extrusions as the particles became available, for the various reactor experiments. The fissile particle cores contain the fissionable material in the reactor, enriched uranium in the form of UC_2. Fissile particles were

TABLE I

DATA ON GLASS-BEAD-LOADED EXTRUSIONS

Batch No.	Matrix Carbon Filler	Appearance	Actual Vol% Beads	Matrix Carbon Density (g/cm^3)
5525	KX-88	Crazed	42	1.62
5526	KX-88, Thermax (85-15)	Crazed	42	1.63
5527	M3	Pebbly	41	1.60
5528	M3, Thermax (85-15)	Rough	43	1.63
5529	S97	Pebbly	41	1.56
5549	S97	Pebbly	39	1.57
5530	S97, Thermax (85-15)	Crazed	42	1.61
5531	1074	Crazed	42	1.63
5545	1074, Thermax (90-100)	Crazed	41	1.65
5532	1074, Thermax (85-15)	Crazed	42	1.64
5546	1074, Thermax (80-20)	Crazed	42	1.63
5550	GP-48	Pebbly	41	1.56
5543	GP-48, Thermax (85-15)	Rough	42	1.58
5551	9553	Pebbly	40	1.56
5544	9553, Thermax (85-15)	Rough	42	1.59

usually of the TRISO design, having a buffer carbon coat next to the core; an inner low-temperature isotropic, i-LTI, carbon coat; a SiC coat; and an outer low-temperature isotropic, o-LTI, carbon coat. Particles made at LASL had a ZrC coat or a ZrC-C graded coat in place of the SiC coat.

The fertile particle cores contain thorium as either ThO_2 or ThC_2. The fertile particles were usually of the BISO design, having a buffer carbon coat and a low-temperature isotropic carbon coat, although some were of the TRISO design described above.

The next series of development extrusions was made using TRISO fertile particles produced by General Atomics (GA) for the Fort St. Vrain (FSV) HTGR. These particles were −20 +24 mesh with an average size of 775-μm diam. Many particles were not spherical, but were faceted, and had crushing strengths averaging 1.8 kg. The extrusions contained 35 vol% FSV fertile particles and 6 vol% fissile-size (~500-μm-diam) carbon shim particles. The purpose of these extrusions was to investigate the effect of extrusion pressure and mixing procedures on the coated particles.

It became obvious after making a few extrusions that some coated particles had been damaged. When the ThC_2 particle cores were exposed to air (moisture), the carbide hydrolyzed and the volume change caused a spall on the extrusion surface. This problem was evident on all extrusions. Later experiments showed these particles to be very susceptible to damage. Extrusion mixes that were hand molded into rods or plates, but never extruded, also showed surface spalls.

Although the crushing strength of the TRISO particles was low, we felt that hand molding or even extrusion shouldn't damage the number of particles indicated by the spalls observed. Other puzzling observations will be mentioned later.

Microradiography of the particles indicated that a high percentage of the SiC coats on the particles were cracked, although both the i-LTI and o-LTI carbon coats appeared to be intact. Very possibly, it would take little pressure to break the carbon coats if the SiC were cracked.

In spite of the shortcomings of the particles, we learned several things and certainly got a feel for the extrusion operation. The following are some specifics that we learned.

(1) Extrusions can be made readily using our existing equipment and fixturing in 1-m lengths with little trouble in relation to straightness or taper.

(2) Extrusion pressures varying by a factor of ~3 were used, with a pressure on the mix of 2 MPa (estimated) considered optimum. It was desirable to keep the extrusion pressure as low as practicable to minimize particle damage.

(3) The number of coated particles damaged during extrusion was related to the extrusion pressure.

(4) The number of coated particles damaged was not related to the number of times a mix was extruded. This was one puzzle we could not rationalize readily.

(5) The number of damaged particles did not appear to increase between the curing operation and the high-temperature heat treatment.

(6) The TRISO-coated particles did not appear to be damaged when heat treated to 2075 K, when they were not in a graphite matrix.

(7) Extrusions loaded with the TRISO particles will continue to deteriorate in laboratory air for a matter of weeks after being made. Some extrusions completely disintegrated.

Particles in an extrusion could be damaged by interaction between the particle coating and the matrix. Other laboratories have observed damaged coatings caused by the matrix's adhering to the coating and damaging the coating when the matrix shrank. We have not seen damage of this type metallographically. In the event that this was happening, particles were coated with wax or fugitive plastic coats before extrusion. Carnauba wax appeared to provide a buffer space between the matrix and the particle. Particle damage was small, observed as surface spalls on the extrusion, but similar to damage to extrusions made without the wax coating on the particles. This was true only when the extrusion pressures were low (2 MPa).

Different methods were available to us for making the extrusion mix. Intensive mixing, like passing the mix through a meat chopper, could not be used because of severe particle damage. Mixes could be made by hand mixing (as was done with all early mixes), by solvent mixing, or by mixing in a Patterson-Kelley twin-shell blender. The blender could be used only if the intensifier speed were

reduced to <1000 rpm to prevent particle damage. All these methods produced similar results in extrudability, physical appearance, particle damage, and matrix density (1.6 g/cm³).

We felt that, without intensive mixing, the binder was not being thoroughly mixed with the matrix carbon. To eliminate this problem, we decided to mix the binder and matrix carbon thoroughly before adding the coated particles to the mix.

The following procedure evolved.

(1) The carbon and 60% of the Varcum to be used are mixed together.
(2) The mixture is passed through a meat chopper twice.
(3) The mixture is extruded using a 1/4-in. tubular die and a 64-to-1 extrusion ratio.
(4) The material again is passed through a meat chopper.
(5) Steps 3 and 4 are repeated.
(6) A third of the remaining Varcum, 13-1/3% of the total, is added to the mix and mixed by hand.
(7) The material is passed through a meat chopper twice.
(8) Steps 3 and 4 are repeated twice.
(9) Steps 6, 7, 3, 4, and 5 are repeated twice.

The mix at this stage is very wet as it contains the total Varcum for the particle (41 vol%) loaded mix. An excess of the carbon-binder mix has been made to provide a sufficiently large batch for thorough mixing. All particles going into the mix have been bottle blended for 15 min and then hand blended for 10 min with an appropriate amount of the matrix mix. The viscosity of this mixture is then proper for the extrusion operation.

When this mixing procedure was used, matrix densities increased to 1.65 g/cm³ or more.

Two sets of compacts (lots 006 and 007 with nine compacts in each set) were made for irradiation experiment OF-2 in the Oak Ridge Reactor (ORR). The compacts contained both fissile and fertile coated particles. One compact from each set was used in the irradiation studies.

The compacts were 15.75 ± 0.05 mm in diameter and 12.7 ± 0.25 mm long. Each 006 compact contained 0.035 g ^{235}U and 0.63 g thorium and each 007 compact contained 0.053 g ^{235}U and 1.095 g thorium. Half the ^{235}U was added to the pressing mix as GA TRISO fissile particles and half as LASL particles having a ZrC-C graded coat. All the thorium was added as GA BISO fertile particles. Spherical carbon shim particles were added to the mix to bring the total amount of particles in the compacts to 41 vol%.

The matrix carbon in the compacts consisted of M3 graphite flour (−60 mesh) and carbon from the Varcum binder. The graphite flour and the Varcum were mixed in a series of operations where the mixture was passed alternately through a meat chopper and extruded (six times) as described previously. All the coated particles and carbon shim particles required in the mix were blended together. They were then hand mixed with the proper amount of the M3-Varcum mixture.

Weighed portions of the mix were placed in a 16.16-mm-diam slug die and pressed under a 91-kg load. The compacts were placed on a stainless steel plate and covered with aluminum foil for curing.

Seven compacts from each set were cured and eventually heat treated to 2075 K. Two compacts from each set were placed in acetone after being pressed and weighed, to wash the binder from the particles and graphite. The particles were separated from the graphite by screening. This procedure gave us a check on the weight of particles in the compacts. In the 006 compacts, the weight was 0.7% less than calculated and in the 007 compacts, it was 1.3% more than calculated. These weights were acceptable considering the small batch sizes we were using and considering that the particles and graphite-Varcum mixture were mixed by hand.

The heat-treated compacts were weighed and measured. All of the 006 and three of the 007 compacts were within the dimensional tolerance. All compacts were radiographed and gamma counted by LASL Group M-1 and leached by LASL Group CMB-3 to remove any exposed uranium or thorium. After leaching, they were gamma counted again. Two compacts from each set were sent to the Oak Ridge National Laboratory (ORNL) and one from each set was tested in the ORR. One of the remaining compacts from each set was examined metallographically (LASL Group CMB-8) and one was analyzed chemically. The chemical analysis served to calibrate the gamma count data.

Leaching losses were very low and metallography indicated no damaged particles or cracks.

The irradiation samples were run at full HTGR fluence at a temperature >1525 K. Postirradiation examination showed no visible matrix change and no matrix-particle interaction.

Extrusion work continued with two changes. A new bronze extrusion die having a streamlined entrance (a concave radius followed by a convex radius) and a 13-mm-diam straight section (outlet) was used. Also, extrusions were made in which the TRISO particles were replaced with spherical carbon particles having a similar size, −20 +24 mesh.

The new die worked very well with no extrusion flaws that could be attributed to the die. With the low extrusion pressures that we use, die design is not a major concern in this program.

One point of interest that has never been resolved is that mixes containing 35 vol% spherical carbon particles required about twice the pressure to extrude as mixes containing 35 vol% TRISO fertile particles. The amount of binder was the same in all cases. Obviously, something about the particle surface is affecting the extrusion pressure. Possibly the carbon particles are porous and are absorbing binder.

Two extrusions, BO-1 and BO-2, contained 6 vol% FSV fissile coated particles and 35 vol% spherical carbon particles. After the extrusions were processed to 2075 K, they were leached at 1225 K for 8 h in a mixture of Cl_2 and CO. There was no weight loss, indicating that there was no serious coated-particle damage. It was encouraging to know that extrusions could be made with little or no particle damage when the extrusion pressures were reasonable (2 MPa) and the coated particles were relatively strong. These particles had a crushing strength averaging 2.8 kg.

The Great Lakes Carbon Corp. (GLCC) H-451 graphite is one of the materials proposed for HTGR fuel elements. Machining chips of this graphite were obtained, ground, and classified into various screen fractions. The proper amounts of the various screen fractions were reconstituted to duplicate the screen analysis of the −60 mesh M3 graphite flour used in most particle-loaded extrusions. Extrusions were made, using the H-451 flour, and were processed to 2075 K. Densities were a little less than for similar extrusions made with the M3 flour.

The screen analysis on a batch of H-451 flour was changed to include the −35 +60 mesh fraction to see if the coarse particles would offer some advantage when mixed with the coarse coated particles. The mix (41 vol% coated particles) extruded easily, but the density was a little less than that of the extrusion made with the −60 mesh flour.

One part of this development program not completed was the investigation of graphite filler particle size, shape, and density, and their effect on matrix density and matrix cracks. The elimination of matrix cracks, although desirable, may be more an aesthetic goal than a practical necessity.

HFIR EXPERIMENT HT-31 EXTRUSIONS

Samples from three different LASL extrusion batches were required for the High-Fluence Isotope Reactor (HFIR) HT-31 irradiation behavior experiment. These samples were the first fueled extrusions supplied by LASL for such a test.

The specimens were 9.78 mm in diameter and 21.34 mm long. The specimens could not be machined on the diameter because of excessive particle damage. Therefore, the diameter was obtained by having a die of the proper size and obtaining predictable shrinkage during heat treatment.

All extrusions contained 6 vol% fissile TRISO-coated particles supplied by ORNL, 2 vol% fertile BISO-coated particles obtained from GA, and 33 vol% carbon particles with ZrC and ZrC-doped carbon coatings provided by LASL Group CMB-8.

One extrusion, SNM6517-01, had as a matrix filler 85 parts M3 graphite flour and 15 parts Thermax. The Thermax was added to increase the matrix density although, as explained earlier, the addition results in some surface crazing and matrix cracks.

The second extrusion was made to determine the feasibility of keeping the particles detached from the matrix and thus eliminating particle-matrix interaction, which could result in particle damage. This extrusion, SNM6517-02, was the same as the first except that all particles were coated with a thin layer of carnauba wax. The coating prevented the Varcum binder from wetting the surface of the coated particle during the extrusion and cure cycle. All vestiges of the wax were removed during heat treatment.

The Airco Speer Carbon-Graphite Division of Airco, Inc., (A-SCC) has supplied LASL with a small quantity of S-0969 graphite flour. This flour is used by A-SCC to manufacture graphite sticks supplied to GA for HTGR fuel element development. The third extrusion for the radiation experiment, SNM6517-03, was made using the S-0969 graphite flour instead of the M3.

Carbon particles were used as prototype fissile, fertile, and inert particles for extrusion development for the HT-31 experiment. Appropriately sized Kreha carbon particles, which had been heat treated to 2470 K, were used. Because there were only sufficient fissile coated particles for the three HT-31 experiment extrusions, all mix development and determination of matrix densities for compositional control were done with prototype particles. This turned out to be a bad situation as problems that were not evident in the developmental extrusions showed up in the HT-31 extrusions. For example, visual examination of the heat-treated extrusions made for HT-31 showed that the outer surface was crazed more than normal. Metallographic examination of the three extrusions showed large cracks and the two extrusions without the wax-coated particles showed microcracks throughout the structure. The matrix densities were ~10% lower than anticipated, averaging 1.61 g/cm^3. The fissile particles from ORNL had crushing strengths averaging 2.59 kg. However, we observed that the carbon coatings on some particles cracked at pressures as low as 1.09 kg. Such particles are too weak to withstand the extrusion operation. Evidence of damaged particles was seen when some broken carbon shells were found in the −35 +65 mesh fraction of the extrusion residues, which had been washed with acetone to remove the binder.

All specimens were leached and, if we assume that all leaching losses were due to loss of uranium (UO_2), ~25% of the uranium could have been lost. These specimens contained about three times as much thorium as uranium. Chemical analyses indicated that ~10% of the uranium was lost and that the thorium content was about as anticipated. Difficulty was encountered with the chemical analyses. A sampling problem was identified in that a specimen or the part of a specimen analyzed was too small to represent the analysis of the extrusion batch. This problem was of special concern in the HT-32 samples discussed later.

It is imperative that sufficient coated particles of the type to be used in extrusion for reactor experiments be available for complete evaluation in developmental extrusions. The specimens made for HFIR test HT-31 were irradiated at about 9 x 10^{21} nvt at 1525 K.[4]

Figures 1 and 2 show samples of one fuel rod before and after irradiation. Some of the cores have been lost because of the metallographic polishing. The graphite matrix showed little or no effect attributable to the irradiation.

HFIR EXPERIMENT HT-32 EXTRUSIONS

Development extrusions for HT-32 were made using coated particles recovered from the residues of the HT-31 extrusions. The residues, not heat treated, were washed with acetone to remove the Varcum binder. The dried residue was then screened to separate the particles from the graphite flour.

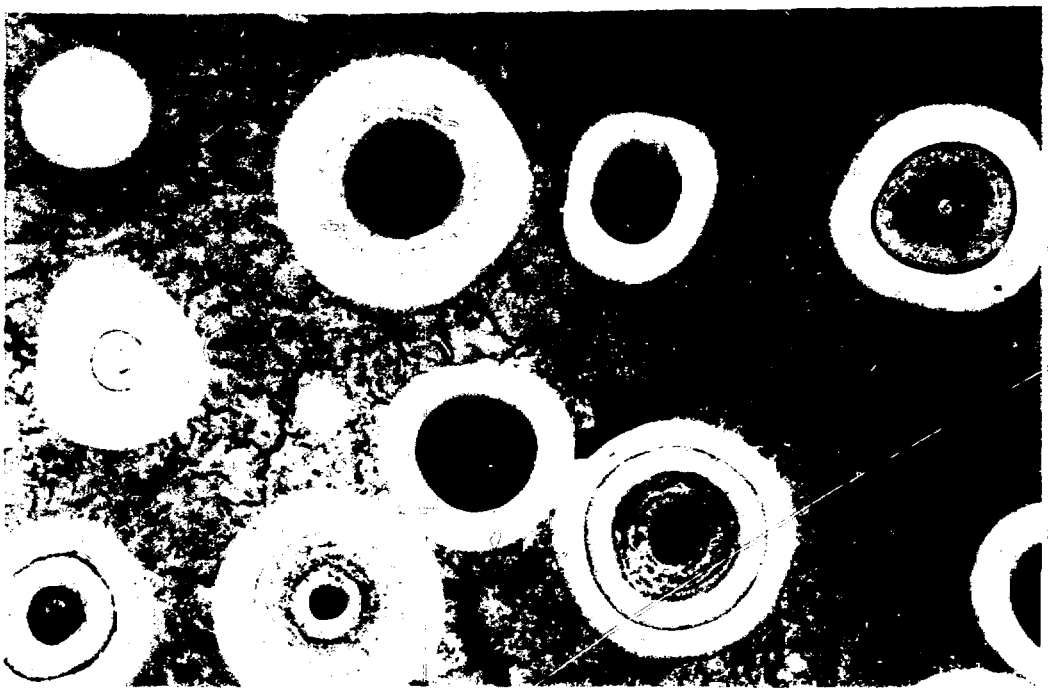
Further extrusion development work was done using carbon-coated carbon particles supplied by LASL Group CMB-8. These particles were originally made to be used as shim particles for HT-32, but the coatings turned out to be slightly optically anisotropic so the particles were used for development. The extrusions containing these particles looked better and had >4% higher matrix densities than development extrusions made with the reclaimed HT-31 particles. Again, development results are strongly dependent on the particles used.

Three particle-loaded extrusions were made to supply irradiation specimens for HT-32. These specimens were the same size as those furnished for HT-31.

The matrix of the first extrusion, NM6517-01, contained M3 graphite flour without Thermax. The matrix of the second extrusion, NM6517-02, contained 90 parts M3 flour and 10 parts fine (0.6-μm) graphite flour. The fine flour was added to improve the packing density of the matrix carbon and also to increase the amount of graphitic material in the matrix. Both extrusions were heat treated using the conventional long cycles of 60 h to 523 K (cure) and 48 h from 473 to 1075 K (bake).

The third extrusion, NM6517-03, had the same composition as the first extrusion and was processed using fast heating cycles. The curing cycle was 15 h

(a)



(b)

Fig. 1.
LASL heat-treated fuel rod SNM6517-03. Magnification: (a) ~9X, (b) ~50X.

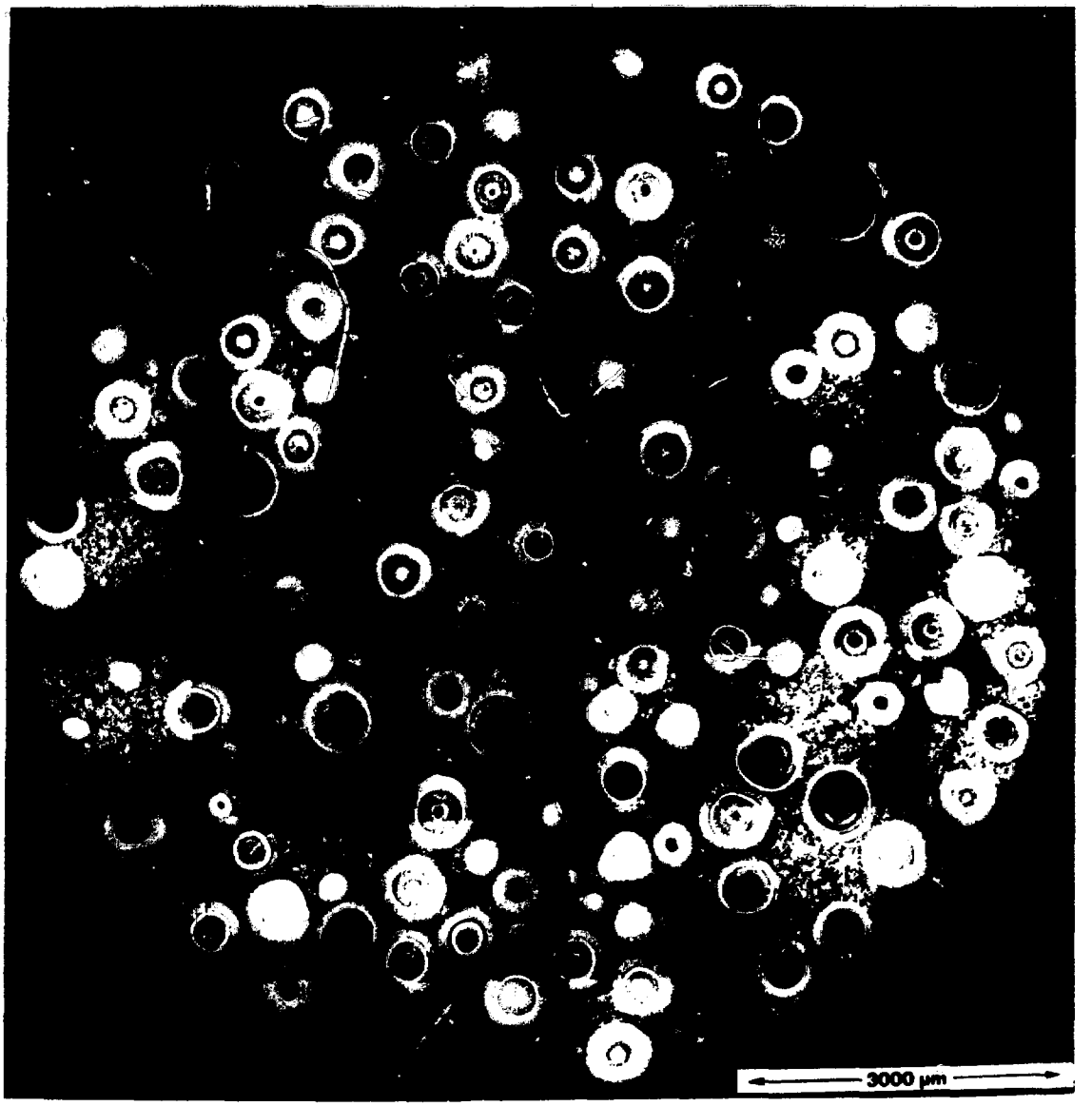


Fig. 2.
LASL fuel rod SNM6517-03 after 9.0 x 10^{21} nvt at 1523 K. (Courtesy of Oak Ridge National Laboratory.)

and the baking cycle was 6 h. All extrusions were heat treated to 2075 K, allowing 5 h to temperature with a 1-h hold. The same extrusion could not be used for the normal and fast heat-treating experiments because the shrinkage was different. The shrinkage during the fast heating cycles was less than when the conventional cycles were used, therefore the extrusion die for NM6517-03 was 0.05 mm (0.002 in.) smaller than the die used for NM6517-01, which was 10.06-mm diam.

Extrusions NM6517-01 and -03 looked good after processing but the surface of extrusion NM6517-02 was slightly crazed.

All extrusions contained coated fissile particles from ORNL, which were the same as those used in the HT-31 extrusions. However, instead of using GA

fertile particles as was done in HT-31, two lots of coated fertile particles made by LASL Group CMB-8 were used. Also, three lots of carbon shim particles coated by LASL Group CMB-8 were used to bring the total volume of coated particles in the extrusions up to 41 vol%.

All HT-32 specimens were machined on the ends only, were leached, and samples were submitted for chemical analyses. The analyses indicated that the thorium content varied from 0.023 to 0.048 g/cm³ of sample. The desired loading was 0.041 g Th/cm³. This variation is intolerable. Part of the problem may have been the technique used to obtain the chemical sample. Each irradiation sample is quite small, only 1.6 cm³, and only a portion of the sample was used for the chemical analysis. In a material such as this, loaded with a relatively few large particles, a representative sample may have to contain several cubic centimeters.

Experiments were started to determine the uniformity of loading of our extrusions.

Extrusions 5881 Th and 5882 Th were made to check the uniformity of the thorium distribution throughout the length of an extrusion. Batch 5881 Th contained BISO fertile particles, whereas batch 5882 Th contained LASL Group CMB-8 lots 78 and 94 TRISO particles. Both batches supposedly contained the same concentration of thorium. However, 5882 Th contained many more thorium particles because the thorium concentration in the particles was lower. The BISO particles contained 58.87% thorium, lot 78 contained 9.57% thorium, and lot 94 contained 10.23% thorium. Both batches contained shim particles to bring the total volume of particles up to 41%.

Each batch was mixed and extruded in the normal manner and cut into 20 samples. The samples were numbered in sequence as they emerged from the extrusion die. Ten 20-mm-long, even-numbered samples, taken from throughout the length of each extrusion, were cured, baked, and gamma counted at LASL Group M-1. Counting time was 10 min for each sample. The samples were fired to 2075 K for 1 h. They were measured to determine shrinkage and density as shown in Tables II and III.

The ~140-mm-long, odd-numbered samples, from between the short samples, were washed in acetone, and the particles in each sample were screened from the graphite flour and weighed.

TABLE II

5881 TH SAMPLE DENSITY[a]

No.	Density (g/cm³)
2	1.69
4	1.69
6	1.70
8	1.71
10	1.70

[a]The desired density was 1.70 g/cm³. The average diameter was 9.72 mm and the average longitudinal shrinkage was 3.15%.

TABLE III

5882 Th SAMPLE DENSITY[a]

No.	Density (g/cm³)
2	1.85
4	1.86
6	1.87
8	1.86
10	1.87

[a]The desired density was 1.86 g/cm³. The average diameter was 9.73 mm and the average longitudinal shrinkage was 3.17%.

Assuming that the samples that were washed and screened would have had similar shrinkages and densities, we can calculate the particle volume in the extrusion. Nonuniform particle distribution or segregation of light and heavy particles would show up as variations in the volume percentage of particles. Obviously, samples this long are quite uniform, as shown in Table IV. One inherent error in this measurement is that the volume of the dissolved sample is based on a measurement of the sample length in the green condition. It is difficult to make an accurate measurement on the uncured material.

The target volume percent was, as before, 41. Any deviation from this number simply reflects a different shrinkage than was anticipated. Variations

TABLE IV

TOTAL VOLUME PERCENTAGE OF PARTICLES

5881 Th	
No.	Vol%
1	41.4
3	41.4
5	41.6
7	41.4
9	41.2

5882 Th	
1	41.6
3	40.7
5	41.3
7	41.2
9	41.0

from an average are due in part to nonuniform particle loading, as explained earlier. Obviously, in samples this large these differences are very small. We are looking for large errors, 10 to 50% of the total loading.

The ten even-numbered samples, similar in volume to an HT-32 sample, were gamma counted at LASL Group M-1. Samples from batch 5881 Th loaded with BISO particles, but with fewer particles, had a standard deviation about a mean, in the gamma counts per gram of sample, of 10.5%. The deviation in the samples from batch 5882 Th was only 2.2%, indicating that the larger number of thorium-containing particles in this material greatly improved the loading uniformity. One puzzle was not readily explained. The actual gamma counts in 5882 Th were 2-1/2 times the counts in 5881 Th. Apparently, the source of the thorium was different in each case and the difference in gamma count was due to decay products (daughter elements) present.

Samples of 5881 Th and 5882 Th, which gave the high and low extremes of gamma count, were burned in air and the ThO_2 kernels were recovered. The weights of the kernels indicated that the thorium loading in both batches was close to the 0.041 g/cm³ desired. In batch 5881 Th loaded with BISO particles, it takes only about 70 particles/cm³ to obtain this loading. Getting a uniform dispersion of this small number of particles in an extrusion mix is very difficult. On the other hand, in batch 5882 Th loaded with LASL Group CMB-8 TRISO particles having smaller ThO_2 cores, similar to the HT-32 samples, we estimate that there are six times as many particles/cm³ for the same thorium content, which is confirmed by improved loading uniformity.

Batch 5884 Th was made to check the uniformity of thorium along the length of an extrusion and to see if multiple extrusions improved the uniformity. The batch contained 0.041 g of Th/cm³, the same as batches 5881 Th and 5882 Th. The thorium was added to the extrusion mix as BISO particles having relatively large ThO_2 cores.

The 5884 Th batch was mixed in the normal manner and extruded once. The extrusion, 1575 mm (62 in.) long, was divided into 15 pieces and a 25-mm sample taken from each piece. The 15 samples were each weighed and placed in plastic containers. The containers were then taken to LASL Group M-1, where the gamma radiation was counted for 100 s. The samples were returned to LASL Group CMB-6, where they were combined with the rest of the extrusion, hand mixed, and extruded. The heel was left in the press, so on the second and subsequent extrusions the first 460 mm of extrusion were not sampled. The remainder of the extrusion was divided into 15 pieces and again 25-mm samples were taken from these pieces. These samples were handled exactly as the first samples. This operation was repeated through four extrusions. Extrusion No. 5 was not sampled, No. 6 was sampled and counted, No. 7 was not sampled, and No. 8 was sampled and counted. Extrusion No. 9 was partially cured and partially washed in acetone to obtain the particle weight and thus the particle volume.

The gamma count data are shown in Table V.

The counts per gram continue to rise with each extrusion. This rise could be due in part to loss of Varcum binder each time a vacuum is applied to the mix before extrusion. Obviously, extruding does not improve sample uniformity, at least for these small samples.

Samples for chemical analyses taken from the original extrusions made for HFIR HT-32 contained a volume less than that of one irradiation sample, as

TABLE V

GAMMA COUNT DATA ON BATCH 5884 Th

No. Times Extruded	Avg. Counts/g of Sample	Std Dev about a Mean %
1	1258	6.4
2	1316	9.1
3	1343	7.1
4	1353	8.1
6	1371	7.3
8	1420	8.1

explained previously. These analyses showed considerable scatter in the thorium content. Samples from these extrusions were analyzed again for thorium, only this time a whole HT-32 irradiation specimen (1.6 cm^3) was analyzed. The spread in analyses was 9%, a big improvement over the previous analyses. However, the average analysis was 28% lower than desired. For this reason, the three HT-32 specimens were remade. An excess of thorium was added to the extrusion mix so that the specimen analysis would be correct if 28% of the thorium were lost. The uranium analysis on the HT-32 samples was also low, so an additional 10% uranium was added to the extrusion mix. Just where the uranium and thorium went is not known, as the leaching losses can account for only part of the metal weight. Again, we probably have a sampling problem. Of course, the main purpose of the leaching operation was to eliminate uranium or thorium exposed by the machining operation when the specimens were cut to length. This loss could amount to several percent of the metal in the specimen.

The remade HT-32 specimens, extrusion lots NM6517-04, -05, and -06, had matrix densities averaging 1.63 g/cm^3. As mentioned previously, additional uranium was added to the mix so that, if 20% of the uranium were lost, the uranium content in the specimen would be correct. Actually, this addition was 25% of the desired uranium weight. The HT-32 remake specimens averaged 0.0262 g uranium instead of the 0.02235 g uranium requested, or 17% more. The spread in loading was only ±6%, which was considerably better than the original HT-32 specimens. Also, we probably had a more representative sample at this time.

The thorium content of the specimens averaged 0.0872 g, whereas 0.0662 g was requested for an excess of 32%. Obviously, the faulty analytical data we obtained on previous samples because of sampling problems misguided us in our loading corrections. The thorium loading spread in the three lots was only +2 and −3% of the average.

Specimens were sent to ORNL for irradiation.

HFIR EXPERIMENT HRB-13 EXTRUSIONS

Four particle-loaded extrusions were made to supply irradiation specimens for HFIR experiment HRB-13. The specimens were 12.45 mm in diameter and 9.84 mm long. Two specimens from each extrusion were irradiated. The desired fissile and fertile loadings are shown in Table VI, and the desired volumes of the various particles in the four extrusions are shown in Table VII.

Because of the small specimen size, a considerable fraction of the coated particles in the specimen could be damaged when the specimens were cut to length. We assumed that all particles within one particle diameter of the ends were damaged and would contain no fissile or fertile material. The volume of fissile and fertile particles in the extrusion batch was thus increased, and this

TABLE VI

DESIRED FUEL LOADINGS FOR LASL HRB13 SPECIMENS

Specimen No.	Fissile Loading (g U/cm^3)	Fertile Loading (g Th/cm^3)
HRB 132700	0.02789	0.43141
HRB 132900	0.02911	0.44566
HRB 133700	0.04067	0.53380
HRB 133900	0.04544	0.56777

TABLE VII

COMPOSITIONS OF EXTRUDED AND HEAT-TREATED LASL HRB13 SPECIMENS

Specimen No.	Particle Loadings: Fissile LA149 (vol%)	Fertile GA6291 (vol%)	Shims LA27 (vol%)	Total (vol%)	Matrix (vol%)
HRB 132700	9.12	24.85	7.03	41	59
HRB 132900	9.52	25.68	5.80	41	59
HRB 133700	13.30	30.76		44.06	55.94
HRB 133900	14.86	32.71		47.57	52.43

increase is reflected in the numbers shown in Table VII. Two of the extrusions contain more than the normal 41 vol% particles.

The matrix for three extrusions consisted of M3 graphite flour and the carbon residue from the Varcum binder. The fourth extrusion (series 2700) used GLCC H-451 graphite in the matrix instead of M3. The ground H-451 was screened into various size fractions and proper quantities of each fraction were recombined so that the particle distribution approximated that of the M3 graphite flour.

The fissile particles were made at LASL. The cores were UC_2 and the particles were of the TRISO design containing ZrC (LA 149). The fertile particles were GA BISO (GA6291). The shim particles were spherical carbon particles coated with carbon at LASL (LA 27). All extrusion batches were mixed and extruded using procedures outlined previously.

The extrusions were heat treated using fast heating cycles similar to those used on previous extrusions. However, the high firing temperature was originally set at 2475 K instead of 2075 K. This setting was used to provide further densification of the matrix and possibly to start some orientation of the Varcum carbon to improve the thermal conductivity of the fuel. However, a calibration specimen containing fissile-size shims and fertile particles gave evidence (odor) of carbide formation after a 2475 K high-firing operation. Thermodynamic calculations by Terry Wallace, LASL Group CMB-3, indicated that the reaction $ThO_2 + 2C \longrightarrow ThC + CO_2$ could proceed to the right to some extent above 2405 K. Consequently, to prevent any further reaction, a final firing temperature of 2375 K was chosen.

The HRB-13 extrusion head damage appeared limited to cut surfaces and a few particles that pulled out on the cylindrical extrusion surfaces. Weight losses on leaching verified this conclusion. The samples were leached for 4 h in a Cl_2-CO gas stream at 1225 K to remove exposed uranium and thorium.

The uniformity of the samples was measured by counting gamma emission from adjoining sections of the extruded rods and on the rods cut to sample size, one piece at a time, before and after leaching. Table VIII contains the counts and standard deviations measured on the sample pieces after leaching. Except in the rod made with H-451 flour, both fissile

TABLE VIII

UNIFORMITY OF THE EXTRUSIONS AS MEASURED BY GAMMA COUNTING INDIVIDUAL SECTIONS OF THE EXTRUDED RODS

Extrusion No.	Thorium (counts/min)	Uranium (counts/min)
HRB 132700	133839 ± 4.0%	3925 ± 3.8%
HRB 132900	139069 ± 1.4%	3875 ± 2.5%
HRB 133700	178762 ± 2.6%	4653 ± 2.2%
HRB 133900	195316 ± 2.9%	4907 ± 2.4%

and fertile particles appear to be uniformly distributed within about 2.5%.

Chemical analyses of 1.18-cm^3 samples, the same size as the radiation specimens, again showed that it is very difficult to obtain uniform loadings on small pieces. The uranium loading varied from 8 to 16% above the desired loading, whereas the thorium content varied from 2% below to 14% above the desired loading. No doubt over a longer length (larger sample size) the loadings would be much more uniform as indicated by the gamma counts.

CONCLUSIONS

A process was developed to extrude coated-particle-loaded graphite having high particle loadings (>45 vol%), good dimensional stability, high matrix density (>1.6 g/cm^3), and thermal conductivity much improved over impregnated fuel sticks.[5] It was demonstrated that the metal loading and volume percentage particles in an extruded fuel could be controlled closely and that particle damage was minimal. Current data indicate little or no effect of irradiation on the extrusions.

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