IMPROVED GRAPHITE MATRIX FOR COATED PARTICLE FUEL*

D. Schell, K. Davidson, C. Hollabaugh, R. Reiswig, P. Wagner,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

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 He coolant passages while others contain fuel rods. The fuel rods, around 1.57-cm diam, consist of short, ~ 5-cm-long segments which are made by a molding process. In making the segments a tube is filled with a mixture of spherical particles consisting of coated fissile particles and coated fertile particles to give the desired U and Th loading and carbon shim particles to fill the remaining segment volume. The void between the particles is infiltrated with pitch or a mixture of pitch and a fine graphite flour. The fuel rod segments are heat treated and placed in a fuel channel in the graphite fuel element. The fuel rod matrix is relatively low in density and thus has poor thermal conductivity.

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 an improved coated fuel particle which would increase the temperature capability of the fuel, and the other to incorporate these particles in a dense graphite matrix using an extrusion process. This paper will discuss only the second part of the program, that of incorporating coated particles in an extruded graphite matrix.

An extruded fuel rod could be made in one piece, long enough to fill the fuel channel in an HTGR fuel element; around 75 cm. The fissile and fertile loadings in HTGR fuel rods vary considerably depending on the positions in the reactor. An average fuel rod would contain 41 vol% coated particles and this was selected as the nominal loading in our extrusion experiments. The 41 vol% was the total of 6 vol% fissile particles (~ 550 μm diam) and 35 vol% fertile particles (~ 800 μm diam). Although an actual extruded fuel rod would not contain carbon shim particles, only graphite filler particles, our development extrusions, which were made primarily for irradiation tests in the High Flux Isotope Reactor (HFIR), contained carbon shim particles to keep the loading of 41 vol% particles constant. This was done to simplify the evaluation of experimental variables although loadings as high as 55 vol% particles were made.

Increasing the conductivity of the fuel matrix would allow higher reactor coolant temperatures without increasing the temperature of the fuel particles. Thermal conductivity measurements indicated a factor of 10 improvement of an extruded matrix over a conventional fuel segment.

Experimental Procedure

Extrusions made early in the program contained suitably sized spherical glass beads. These were used until spherical carbon particles and coated particles became available. The extrusions were useful in working out extrusion mix composition, investigating various graphite filler flours and measuring relative matrix densities. Also, some indications of suitable die design, extrusion pressures and relative extrusion strengths were obtained. A partially polymerized furfuryl alcohol, Varcum 8251, used extensively in making extruded graphitic fuels and shapes for the Rover (Nuclear Propulsion Reactor) program,[1] was used as the binder for practically all particle-loaded extrusions. Varcum is a thermosetting resin having a carbon residue, upon heat treatment, of 45%. It is desirable to use a thermosetting resin as the extrusion binder in that upon polymerization the extrusions are easily handled and dimensional stability is maintained.

Several different reactor grade graphite flours were used in these extrusion experiments. They varied both in particle size and shape. Thermax, up to 15 pph, was added to many extrusion mixes.

It became evident very early in this program that there was a serious problem with macrocracks in the matrix created during the heat treatment of the extrusions. The matrix shrinks when heat treated but is restrained by the relatively large unforgiving beads, thus cracking occurs. The finer the graphite the greater was the tendency for cracking. For this reason much of our extrusion work used a relatively coarse, -60 mesh, reactor grade 1008 graphite flour from Great Lakes Carbon Corporation.

The first coated particles which were available to us were made by General Atomics for the Fort St. Vrain HTGR. These were TRISO fertile particles having ThC_2 cores and two pyrolytic carbon coats with a SiC coat in between.

We could not extrude these particles without indications of particle failure. When the ThC_2 cores of the particles were exposed to air (moisture), the carbide hydrolyzed and the volume change caused a spall on the surface of the extrusion. This problem was evident to some degree on all extrusions, even those made at very low extrusion pressures. The load required to crush a particle was rather low, averaging 1.8 kg.

Although we apparently needed a stronger particle for a successful extrusion program, these particles proved to be very useful in investigating mix and extrusion variables. We found that we could readily extrude 12.5-mm-diam rods a meter long with little taper or dimensional variation.

Extrusion pressures varying by a factor of 3 were used with an estimated pressure on the extrusion mix of 2 MPa considered optimum. This pressure provided adequately strong extrusions but minimized particle damage.

A few different die designs were investigated, giving the impression that die design had little or no effect on the quality of the extrusions. This was probably due to the low extrusion pressures.

Heat treating cycles were established to cure and carbonize the thermosetting binder. The final heat treatment was to 2075 K in an Ar atmosphere using a graphite resistance furnace. No deleterious effects were noted on the extrusion or particles due to this heat treating temperature.

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Early extrusion mixes were simply made by hand mixing the appropriate amounts of the various ingredients and particles together. Satisfactory extrusion mixes were also made by solvent mixing or through the use of a Patterson-Kelley twin-shell blender. Intensive mixing could not be used because of particle damage. We found that if the graphite matrix flour and the Varcum binder were intensively mixed together before the particles were added to the mix the matrix density increased a few percent. The intensive mixing was done through a series of grinding operations, using a commercial meat chopper, and extrusions. The coated particles and shim particles, which were previously blended together, were then hand blended into this mix. The mix was usually extruded three or four times with hand mixing between extrusions. A vacuum system on the extrusion press evacuated the extrusion die, chamber and extrusion mix prior to and during extrusion. There were no indications that particle damage was associated with the number of times a mix was extruded. Multiple extrusion did increase the matrix density. Experiments also indicated that the uniformity of the distribution of coated particles in the extrusion mix did not change with multiple extrusions.

Further development work continued using stronger coated particles which had crushing loads averaging 2.8 kg. Particle damage during extrusion and heat treatment did not appear to be a serious problem. Samples of extrusions leached at 1225 K for 8 h in a mixture of Cl_2 and CO showed no weight loss.

It has been reported that coated particles may be damaged by interaction between the outer pyrolytic carbon coat on the particle and the matrix. If the matrix sticks to the coating, the coating may be damaged when the matrix shrinks during thermal treatment or volume changes that occur during irradiation. We found that we could at least partially isolate the particles from the matrix by coating the particles with a fugitive coating prior to extrusion. The coating was applied to the particles using a solvent. Carnauba wax was the preferred coating material in that it gave the most consistent results. In work at LASL we have observed no indications of interaction between the particles and matrix whether the particles had a fugitive coating or not. This includes a few irradiated samples.

Irradiation Specimens

Over a period of about a year, extrusions containing both fissile and fertile coated particles were made for three tests in the HFIR reactor at Oak Ridge. This represented ten separate extrusion batches.

Several extrusions were similar in nature but contained different developmental coated particles. Two extrusions used graphite flours which originated from graphites developed for making HTGR fuel elements. Other extrusions used different heat treating cycles with four of the extrusions being heat treated to 2375 K.

Matrix carbon densities were around 1.63 g/cm^3.

Some problems did occur in making the irradiation specimens. Macrocracks in the matrix appeared when the graphite flour contained an excess of fines. There was no problem, however, with the specimens being adequately strong. The cracks did not change in appearance or affect the irradiation performance of the specimens during full term fluence and temperature conditions.

One problem peculiar to making irradiation specimens was that the diametrical tolerance was tight and it was inadvisable to machine the diameter because of particle damage. This meant that the extrusion die size and shrinkage of the extrusion during heat treatment determined the diameter. The ends of the specimens were machined so it was necessary to leach the specimens prior to irradiation to remove exposed U and Th. Metallography on duplicate specimens did not reveal any damage to the coated particles due to the extrusion or heat treating operations.

Another problem was in obtaining samples for analyses which were representative of the irradiation specimens. The specimens were very small, containing only 1.2 to 1.6 cm^3. Chemically analyzing a portion of a specimen, which was customary, gave erratic results. Analyzing complete duplicate specimens gave much more uniform results. However, the final solution to the problem was to gamma count each specimen for both U and Th. Similar specimens were then selected for chemical analyses and irradiation.

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. It was demonstrated that the metal loading and volume percent particles in an extruded fuel could be closely controlled and that particle damage was minimal.

References

(1) D. H. Schell, J. M. Taub and J. W. Taylor, "The Fabrication of Uranium-Loaded Graphite," LAMS-2587 (1961).