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High-Temperature Fuel Technology for Nuclear Process Heat: ZrC-Containing Coated Particle Fuels and High-Density Graphite Fuel Matrices

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HIGH-TEMPERATURE FUEL TECHNOLOGY FOR NUCLEAR PROCESS HEAT: ZrC-CONTAINING COATED PARTICLE FUELS AND HIGH-DENSITY GRAPHITE FUEL MATRICES

by

Paul Wagner

ABSTRACT

This is the final report on the high-temperature, gas-cooled reactor fuels project that was pursued at the Los Alamos Scientific Laboratory from early 1973 to mid-1977. This work followed two broad paths: (1) ZrC was utilized in various ways to improve the temperature capability of fission-product-retaining coated nuclear fuel particles and (2) techniques were developed for fabricating fuel rods by extruding the coated particles in high-density graphite matrices.

The key to the ZrC coating project proved to be the $ZrCl_4$ powder feeder development. The $ZrCl_4$ reacted with H_2 and CH_4 or C_3H_6 to produce chemically vapor-deposited (CVD) ZrC. This CVD ZrC was used on nuclear fuel particles for replacing the SiC in the TRISO-II design, for making ZrC-C graded coats, and for making ZrC-alloyed isotropic carbon coats. Fuel particles with all of the described coats have been very successful in high-temperature, full-fluence (8×10^{21} n cm^{-2}) irradiation tests. High-temperature diffusion experiments with cesium showed that ZrC is comparable to SiC as a diffusion barrier.

Extruded fuel rods with matrix densities of 1.6 to 1.7 g cm^{-3} and with up to 45-vol% coated particles were made without difficulty. All fuel rods tested in high-temperature, full-fluence irradiations had excellent results.

I. INTRODUCTION AND BACKGROUND

The purpose of this project was to develop improved coated-particle, graphite-matrix nuclear fuels, which could be used in gas-cooled power reactors to obtain the higher coolant outlet temperatures that are required for high-temperature nuclear process heat. We utilized LASL's (Los Alamos Scientific Laboratory) extensive expertise and existing equipment in coated-particle development, graphite research, fabrication of graphite-base fuel bodies, nondestructive testing, and physical-property measurements. The program included (a) design and development of improved fission-product-retaining coated particles to permit increased temperature capability, (b) development of improved fuel rods by extruding commercially available coated particles of contemporary design and improved ZrC-coated particles in high-density graphite, and (c) evaluation of coated particles and fuel bodies by neutron-activation, thermal, and prolonged high-temperature irradiation tests.

The work followed two broad paths:

- Chemically vapor-deposited (CVD) ZrC was utilized in various ways to improve the temperature capability of fission-product-retaining coated particles. Initially, TRISO-II design coated particles with UC_2 kernels and with ZrC coats in place of the SiC were computer designed and made at LASL. These and other particles with ZrC coatings were irradiation-tested at the Oak Ridge National Laboratory (ORNL) as quickly as they could be prepared and arrangements made for the irradiations.
- A continuous process fuel-rod fabrication was studied. Initially these studies were made using commercially available high-temperature, gas-cooled reactor (HTGR) fissile and fertile coated particles. Ultimately LASL-made high-temperature particles were used in the studies. Extrusion methods of fabrication were applied to the development of the coated-particle, graphite-matrix fuel bodies. We studied (a) coated-particle mechanical damage caused by extrusion geometry and volume loading of particles (b) effects of binder, flour, mixing procedures, and use of fugitive solvents for blending and extruding the fuel bodies, and (c) effects of curing, baking, and final heat-treatment conditions. Full-scale extrusions were made to size and evaluated. High-temperature gas-leaching (in Cl_2/CO_2 mixtures) techniques were used for removing exposed heavy metal. These fuel rods were subjected to prolonged high-temperature irradiation tests at ORNL.

Use of the ZrC in place of the SiC permits the use of processing temperatures as high as 2475 K for coated-particle, graphite-matrix fuel bodies. The product of this heat treatment was a dispersion of coated fuel particles in a graphite matrix whose thermal conductivity (at 300 K) was markedly higher [$\lambda \simeq 70-80\ W\ m^{-1}\ K^{-1}$ (Ref. 1)] than that of the fuel sticks in the HTGR ($\lambda \simeq 8-10\ W\ m^{-1}\ K^{-1}$). Such heat-treated fuel rods, if used in an HTGR, would result in higher coolant temperatures without increasing coated-particle operating temperatures or would allow the reactor to operate with current design coolant temperatures at lower coated-particle fuel temperatures.[2]

We have met the anticipated programmatic goals, without exception, and have included additional goals that have proved to be germane to very-high-temperature, gas-cooled reactor (VHTR) systems.

II. THE COATED-PARTICLE PROGRAM

As an early step in the use of ZrC for coated particles, the thermal stress performance of a TRISO-II particle with ZrC in place of SiC was computed using the Dragon Project Stress-2 code.* Using a modulus of 0.4 TPa (6×10^7 psi) for the ZrC, we calculated that for HTGR full-term conditions of 0.74 FIMA (Fraction of Initial Metal Atoms) and a total fluence of $8 \times 10^{21}\ n\ cm^{-2}$ ($E > 0.18$ MeV), there was a safety margin of a factor of 4 in strength (or thickness).

Another early requirement in the ZrC-coated-particle program was modification of existing laboratory equipment and fabrication of new equipment. This was required to meet the dual requirements of pursuing a research and development (R and D) program on fluidized-bed ZrC particle-coating processes and supplying the extrusion facility with a sufficient quantity of particles to pursue the R and D program in fuel-rod extrusion fabrication. The key to the achievement of both goals was the development, fabrication, and operation of the $ZrCl_4$ powder feeder.[3] Details on the construction and use of the 25-mm powder feeder are in the open literature published under the aegis of this program.[4,5] Fluidized-bed coaters of 25- and 76-mm diameter were used (details on the 76-mm coater are in Appendix A). The 25-mm coater was of conventional design, induction heating was used, and temperature measurement was by thermocouples. The 76-mm coater was of similar design utilizing a single nozzle (other coaters of this capacity normally use multiple nozzles or turbulence generators). No particular difficulties were encountered in developing these systems.

There are several ways to use ZrC in particle coats; making discrete ZrC coats, making ZrC-C composite (or alloy) coats, and making ZrC-C graded coats. Our interest in co-depositing ZrC and low-temperature isotropic pyrolytic carbon (LTI) was stimulated by the possibility of making coats with improved thermal and irradiation performance

*We gratefully acknowledge ORNL's cooperation in obtaining this code.

by a simpler fabrication process than that used for the HTGR fissile particles. With a controllable co-deposition process, a continuously graded coat can be made that starts out as pure LTI and has ZrC added in evenly increasing amounts (by reaction of $ZrCl_4$ with the hydrocarbon) until pure ZrC is deposited. The process can then be reversed and the ZrC decreased to get back to the LTI. The stress, which is generated by a mismatch of the thermal expansion coefficients of two adjoining components, would be minimized in such a coat. Such a process would be a single fabrication step and could be used as a substitute for the three separate steps used in the outermost layers of the TRISO-type coated particles. Other advantages to a graded coat could be reduction of the radiation-induced creep in the LTI with a subsequent decrease in the creep-induced stresses in the outermost coats (one of the causes of coat failure at high fluence). The reduction of the magnitude of the physical-properties mismatch achieved by the graded coat would be an additional favorable factor. Addition of ZrC to the LTI eliminates changes in density and Bacon Anisotropy Factor (BAF) in the LTI under high fluence and improves the retention of the solid fission products. The behavior of LASL-made particles having ZrC-doped LTI coats that were irradiated in the ORNL High-Fluence Isotope Reactor (HFIR) HT-31 experiment[6] was excellent. These particles were irradiated at 1525 K to a nominal fluence of 8×10^{21} n cm^{-2} ($E > 0.18$ MeV) with no perceptible changes (macro or micro) as a result of the irradiation. Thus, the potential implied in the use of the ZrC-doped LTI coats is also very great.

These ideas are not necessarily original with LASL. The General Atomic Company, the European Dragon Project, the Austrian group at Seibersdorff, and the Japanese Atomic Energy Research Institute have all tried making ZrC-coated particles. In our discussions with KFA (Kernforshunge Anlage, FRG), the Germans indicated strong interest in the ZrC coats, but in view of the fabrication problems described they have chosen to concentrate on other materials.

The ZrC is made by the reaction of a hydrocarbon gas with a zirconium halide—usually $ZrCl_4$. Quantitative control of the vaporization of the $ZrCl_4$ has been the chief obstacle to the successful co-deposition process in the past. LASL solved this problem by using the described $ZrCl_4$ powder feeder. This method has proved to be controllable and reproducible. Quantitative experiments on preparation of substoichiometric ZrC using the reactions

$$ZrCl_4 + xCH_4 + 2(1\text{-}x)H_2 = ZrC_x + 4HCl$$

and

$$3ZrCl_4 + xC_3H_6 + 3(2\text{-}x)H_2 = 3ZrC_x + 12HCl$$

have been carefully performed and documented.[7-9] LTI graded to ZrC, ZrC graded to LTI, double-graded LTI → ZrC → LTI, and ZrC-alloyed isotropic pyrolytic-carbon coats have been made. A single coating run can produce the single- or the double-graded coat. All of these can be done with no serious problems—the coating process tends to proceed smoothly and coats are laid down as expected from the prerun coating calculations. The ZrC has been made from the reaction between $ZrCl_4$ and C_3H_6, thus utilizing the LTI feed gas throughout (the C_3H_6 is used for the doped co-deposit and for the LTI); it has also been made by switching to CH_4 for the pure ZrC. There is no observable difference between coats made using CH_4 and C_3H_6.

Process parameters for fabrication of ZrC_x have been identified quantitatively and documented.[6,8] Experiments designed to identify the critical process parameters for the ZrC-alloyed LTIs have been reported.[9] These latter experiments are very complex and probably could not have been done without the powder feeder. The actual coating-run data have also been documented.[10]

III. THE GRAPHITE-EXTRUSION PROGRAM

This part of the effort was also very successful.[11] Extrusion of coated particles into high-density graphite matrices is a demonstrated LASL capability [the Rover and UHTREX (Ultra-High-Temperature Reactor Experiment) reactor fuels were made in this manner.] That this technology could be applied to HTGR and very-high-temperature reactor (VHTR) fuels has been amply demonstrated. The thermal properties of these fuels have been as predicted,[12] and the observed irradiation behavior has been exemplary. Our views on the viability and behavior of the high-thermal-conductivity graphite matrix fuels for high-temperature, gas-cooled reactor applications are set forth in Appendix B. The fabrication process has been shown to be amenable to drastic decreases in heat-treatment times and suitable for high-capacity fuel-rod production. Coated-particle volume loadings of 45% were made for the ORNL HRB-13 experiment without difficulty. Thus far, our experience in making extruded fuels encourages us to think that the upper limit to the extrusion process may be the limit due to random particle packing (i.e., the same limit imposed on the injection-molding method).

IV. CESIUM DIFFUSION IN ZrC

To compare the relative effectiveness of ZrC vis-a-vis SiC as a fission-product barrier in fuel structures for high-temperature, gas-cooled reactor applications, a series of cesium infusion experiments on various ZrC powders and ZrC-coated graphite structures was performed to study the cesium solubility, diffusivity, and permeability of this coating material.[13] The ZrC powder results yield a cesium solubility in ZrC of

$$S \text{ (ppm wt)} = 1.7 \times 10^{-6} \exp - [229 \text{ kJ/RT}]$$

over the temperature range (T) 1485-1896 K (R is the gas constant). The diffusion coefficient of cesium in ZrC is 10^{-18} to 10^{-19} m^2/s over a similar temperature interval. The activation energy of diffusion is estimated to be 50 kJ/mole.

The results support the conclusion that ZrC is comparable to SiC as a diffusion barrier to cesium.

V. IRRADIATION RESULTS

Irradiation tests have been performed on LASL's fuel rods or fuel-rod components. These are summarized:

- Fission-gas release tests were performed on LASL-made, ZrC-coated fissile particles in the General Atomic Company (GAC) TRIGA reactor. Values of release divided by birth for these particles were in the 10^{-6} to 10^{-7} range. A value of 10^{-7} is very good.
- HT-28 and HT-29.[14] Three material types, extruded graphite, hot-pressed ZrC, and inert particles with ZrC coats, were irradiated in the ORNL HFIR. All materials performed very well except for one set of particles with double-graded C-ZrC-C coats.
- HRB-12. In this ORNL HFIR experiment, ZrC- and SiC-coated fissile particles are in the same fuel rod. LASL made the ZrC and outer (o) LTI for half the particles; ORNL made the SiC and o LTI for the other half. The postirradiation examination is going on in the ORNL hot cells as this report is being written. We are told that, aside from a slight "peppery" appearance, a preliminary examination shows that the ZrC has been well behaved with respect to radiation damage and fission-product retention.
- HT-31.[9] Materials tested consisted of three extruded fuel rods that contained TRISO fissile particles (made at ORNL) using 6.36% enriched $^{235}UC_2$, ThO_2 BISO fertile particles, and ZrC-containing inert particles with pure ZrC coats and ZrC-doped LTI coats. Nominal test conditions were 8 x 10^{21} n cm^{-2} (E > 0.18 MeV) at 1525 K. All materials behaved very well. To a first approximation, the graphite matrices and the LASL-made particles showed no effects from the irradiation.
- OF-2.[15] Three LASL-made substoichiometric ZrC-coated particles with inert kernels and two high-density molded-graphite fuel rods that contained LASL-made ZrC-coated fissile particles were irradiated in the Oak Ridge Research Reactor test OF-2. The severest test conditions were 8.36 x 10^{21} n cm^{-2} (E > 0.18 MeV) at 1625 K. The graphite matrix showed no effect of the irradiation. There was no interaction between the matrix and any of the particle coats. The loose ZrC-coated particles with inert kernels showed no irradiation effect. The graded ZrC-C coats on the fissile particles were cracked. It is postulated that the cracking is associated with the low LTI deposition rate and is not related to the ZrC.
- HT-32. Three LASL extruded fuel rods using LASL fertile ZrC-TRISO particles are being tested. No Thermax* was used in the fuel-rod matrices.

*R. T. Vanderbilt Co., Inc., New York, NY 10017.

One of the rods was made using an accelerated 2-day total heat-treatment schedule. Irradiation started in October 1976, and there are no reported results at the time this report is being written.

- HRB-13. Eight LASL extruded fuel rods are being tested. LASL ZrC-containing fissile TRISO particles with ZrC coats and ZrC-doped LTIs were employed. All fuel rods were heat-treated using the 2-day heat-treatment schedule. The maximum fuel-rod heat-treatment temperature was 2375 K. Irradiation started in October 1976, and there are no reported results yet.

VI. DOCUMENTATION OF THE PROJECT

As the project advanced, significant accomplishments were written up and published as journal articles or as LA reports (TID-4500 UC-77 distribution). When the subject matter was of general scientific interest and also of direct interest to those involved with gas-cooled reactors, it was published both ways. The reference list includes all the 15 reports and articles that were written on the project. With two appendixes, one on the 76-mm coater and the other on graphite thermal conductivity, this final report completes the documentation of the work that was done.

VII. CONCLUDING REMARKS

From early 1973 until mid-1977 we worked on the VHTR advanced fuels. This project was initiated by LASL and later funded by the US Atomic Energy Commission—Energy Research and Development Administration (AEC-ERDA). Overall, the results of the laboratory work on the particle fuels, the extrusion work on the fuel rods, and the available results of the irradiation tests far exceeded our expectations. This work was done with the GAC-HTGR design in mind and the technology developed could be applied today to the HTGR with no modification whatever of the basic core design. Use of the LASL extruded fuel in the HTGR would increase the mean gas exit temperature at least 100 K with an attendant increase in thermal (and plant) efficiency. This ΔT is based on a conservative thermal analysis of the HTGR core.[2] Because the ZrC-coated fuels are also capable of higher operating temperatures than the fuels now used, still higher gas exit temperatures could be achieved by using these fuels. For use of a prismatic core reactor in a nuclear process heat system, the ZrC-coated particle fuel and the high-density, high-thermal-conductivity fuel matrix are essential if the process temperatures necessary for iron-ore reduction and water-splitting are to be reached.

Another desirable aspect of the extrusion technique is economic. The graphite industry finds continuous extrusion methods for dry-cell electrodes more economical than molding the individual electrodes. Many standard-size electrodes made this way are not largely different in size from the HTGR fuel rods. By analogy, a continuous extrusion process for the fuel rods would be more economical than the individual fuel-rod moldings now contemplated for the HTGR.

We have tried, in this report and in the other project documentation, to present a complete description of the fabrication technology, laboratory behavior, high-temperature irradiation behavior, and operating promise of the ZrC-coated particle fuels and the high-density graphite fuel rods.

ACKNOWLEDGMENTS

This was a complex project and there was considerable interaction with other organizations and people. Significant contributions to the project were made by personnel from the General Atomic Company HTGR Project, the European Dragon Project, KFA of the Federal Republic of Germany, and the ERDA Headquarters staff.

Personnel at the Oak Ridge National Laboratory were especially helpful in planning, performing, and doing the postirradiation examination for the irradiation experiments. In particular, the help of J. H. Coobs, F. J. Homan, W. P. Eatherly, R. L. Beatty, E. L. Long, Jr., T. N. Tiegs, and the ORNL hot-cell crew was invaluable to the program; their aid and encouragement is gratefully acknowledged.

LASL personnel who participated actively in this program were R. J. Bard, C. M. Hollabaugh, R. W. White, L. A. Wahman, R. D. Reiswig, J. A. O'Rourke, L. E. Lanham, W. A. Stark, Jr., K. V. Davidson, D. H. Schell, and P. Wagner. The success

of the program is due in equal part to each of these scientists.

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APPENDIX A

76-mm COATER

As the fuels program progressed, the need for a coater with the capability of satisfying the needs of the extrusion portion became increasingly evident. With this in mind, we designed and built a 76-mm-diam coater. An isometric view of the coater, gas manifold, and $ZrCl_4$ powder feeder is shown in Fig. A-1. The coater itself is made of graphite; a single nozzle with a 60° cone is used for fluidizing the bed. Temperature control is accomplished with a 50-kW, 10-kHz induction power supply. Two nozzle inlets are used; 6.4 mm for carbon coating and 9.5 mm for ZrC coating. The maximum coater temperature is about 1825 K. The coater has been completed for about 1 yr and has been productive for about 7 months.

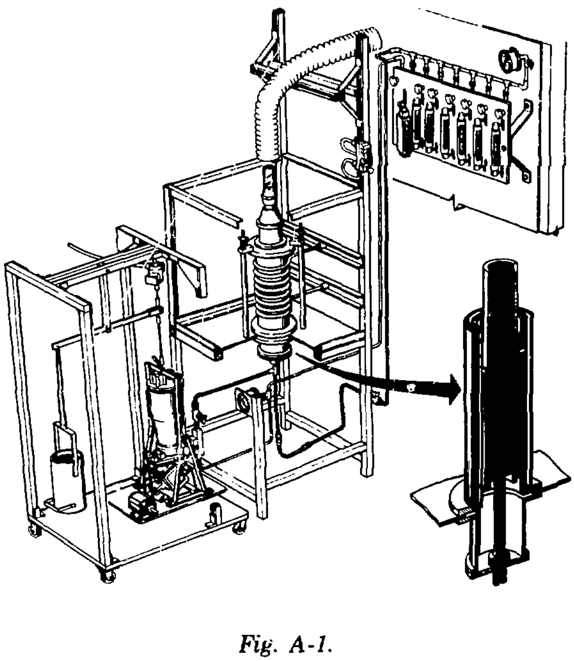

Fig. A-1.
LASL 76-mm coater showing coater, gas manifold, and $ZrCl_4$ powder feeder.

To date, the coater has been used for coating both low-density (carbon) and high-density (ThO_2) kernels. These have been coated successfully in sizes from 175 to 700 μm in diameter. These particles have been coated with buffer coats, inner and outer LTIs, ZrC, graded ZrC, and ZrC-C composites. Particles coated in the 76-mm coater and supplied to the extrusion effort have been inert shims of fissile and fertile sizes, shim particles that were used for materials tests in irradiations (i.e., inert particles with ZrC coats in some form), and ZrC-coated ThO_2 particles that will be used in the HT-32 fuel-rod irradiations. Specialized jobs such as coating the particles for the cesium diffusion experiments have also been done in this coater.

Overall, the coater can make seven coating runs in 10 days on the average. This amounts to about a liter of coated particles every 2 weeks. Because a typical extrusion mix is about 200 cm^3 and the particles take up 40 vol%, or 80 cm^3, 2 week's production can supply enough particles for 12 extrusions. Extrusions in which the particle content is diluted with shims can be made in proportionately larger numbers. Except for occasional mechanical failures, which require shutdown of the coater, operating experience with the 76-mm coater has been quite satisfactory. Normally, all of the product of a coating run is acceptable, suggesting that the fluidization and agitation in the coater is uniform.

The ZrC is deposited at 0.003-0.005 μm/s and a typical ZrC-coating experiment will last about 2 h at the coating temperature. Satisfactory ZrC coats have been made with both CH_4 and C_3H_8 in the 76-mm coater. These do not have any obvious structural differences. Other coats (LTI, ZrC-doped LTI, buffer) have also been made effectively in the coater.

APPENDIX B

THERMAL CONDUCTIVITY OF EXTRUDED HIGH-DENSITY GRAPHITIZED FUEL RODS

I. INTRODUCTION

The logic of the high-temperature fuels program is based on the desirability of using coated-particle fuels that have been incorporated into high-thermal-conductivity (λ) graphite matrices in high-temperature gas-cooled reactors (GCRs). As the program has progressed and experimental data have become available, this logic has been continually re-examined. The goal of making a high-temperature fuel that retains a significant λ advantage over fuels now in use despite the hostile thermal and radiation environment of an operating GCR has been the focus of this scrutiny. In general, the high-density graphite matrices seem to behave as well or better than had been anticipated at the start of the program. This is a brief discussion of the current thinking and some estimates on the behavior of the graphite matrices being used in the high-temperature fuels program.

At the onset, it was clear that graphite matrices could be made using existing extrusion methods and materials with room-temperature thermal conductivities in the region 50-100 W m^{-1} K^{-1} (λ for pitch-injected fuel rods is about 7 W m^{-1} K^{-1} at 300 K). This, however, is true only if the graphite can be heat-treated to a temperature that will allow the binder phase to graphitize* enough to become a good thermal conductor.

The mechanism for this improvement of thermal conductivity in graphite may be illustrated by the following example. Consider the thermal conductivity of an artificial graphite consisting of particles of a well-graphitized material that have been coated with a hydrocarbon binder and that has been heated to a temperature of 2075 K. This is a two-phase system in which the binder is the continuous phase and the graphite particles are the discontinuous phase. The binder has a λ at 300 K of 7-10 W m^{-1} K^{-1} (Ref. 1) and thus will be the major thermal resistance in the graphite. Heat treatment at higher temperatures allows the binder to graphitize and λ to increase. We ran experiments to quantify this.[1] In the graphites used, increasing the heat-treatment temperatures from 2075 to 2475 K increased λ (300 K) of the polyfurfuryl alcohol (PFA) from about 10 W m^{-1} K^{-1} to 25 W m^{-1} K^{-1}, which was, in turn, effective in raising λ (300 K) for the graphite from about 65 W m^{-1} K^{-1} to about 80 W m^{-1} K^{-1} (See Fig. B-1).

Once the decision to use the high-density, high-thermal-conductivity graphite as a fuel matrix has been made, the questions to be addressed are:

(a) Can it be made as a coated-particle fuel matrix?

(b) What is the net effect of temperature on λ for this matrix compared with that for the pitch-injected fuel rods?

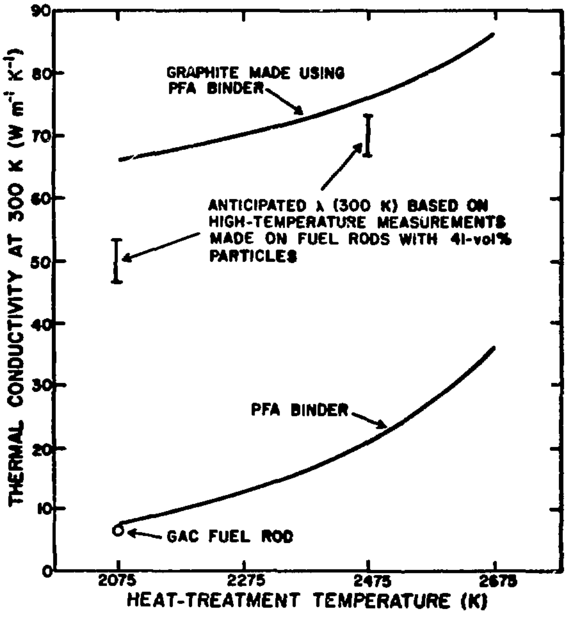

Fig. B-1.
Effect of heat-treatment temperature on thermal conductivity of some graphitic materials.

*Graphite that has been preheated to ~3000 K allowing the structure to develop and form a highly crystalline material. Reasonably isotropic graphites made this way have thermal conductivities >100 W m^{-1} K^{-1}.

(c) What is the net effect on λ of irradiation on this matrix compared with that for the pitch-injected fuel rods?

(d) When the combined effects are considered, does the graphitized matrix have an operational advantage over the pitch-injected fuel rods?

II. EXTRUDED FUEL RODS

The answer to the first question, that of coated-particle graphite matrix fabrication, has been effectively demonstrated. Although fuel-rod development has been done using 41-vol% (the mean HTGR core loading) coated particles in the fuel rods, we estimate that, by using methods and materials thus far employed, fuel rods with 50-vol% coated particles can also be made. The 41-vol% fuel rods have matrix densities of about 1.65 g cm^{-3}. The anticipated 300-K thermal conductivities are about 50 W m^{-1} K^{-1} when heat-treated at 2075 K and about 70 W m^{-1} K^{-1} when heat-treated at 2475 K (see Fig. B-1).

III. EFFECT OF TEMPERATURE

To examine the effect of temperature on λ for a 41-vol% particle-loaded fuel rod, λ was measured in the region 1475-1875 K. A radial heat-flow method[2] was used to obtain λ in a direction perpendicular to the fuel-rod extrusion axis. This is the heat-flow direction in the prismatic block configuration. The thermal conductivity in this temperature region was about 20 W m^{-1} K^{-1} for a fuel rod heat-treated at 2075 K. After heat treatment at 2475 K, λ measured at 1775 K was about 26 W m^{-1} K^{-1}. For artificial graphites made using a PFA binder, with a matrix density of 1.65 W m^{-1} K^{-1}, an effective crystallite height, L_c, in the matrix of ~300+ Å, d_{002} = 3.36 Å, a BAF of 1.3, and an electrical resistivity of 2000 μΩ cm at 1775 K, the value of λ at 300 K is 2-1/2 to 3 times its value at 1775 K.[3] This corresponds to a λ (300 K) of 50 W m^{-1} K^{-1} for a fuel rod heat-treated at 2075 K and 65-75 W m^{-1} K^{-1} for one heat-treated at 2475 K. The pitch-injected-type fuel rod has λ (300 K) in the region 7-10 W m^{-1} K^{-1} and a modest decrease with temperature. LASL systems analysis studies[4] on HTGR have used a temperature-independent λ = 6.9 W m^{-1} K^{-1} for the pitch-injected fuel rods.

It is clear that high-density, well-graphitized fuel rod matrices possess a thermal conductivity advantage of at least a factor of 3-4 over pitch-injected fuel rods at 1775 K. This advantage should be even greater at lower temperatures.

IV. EFFECT OF IRRADIATION

The effect of irradiation on a high-density graphite matrix of the type discussed is to decrease λ. Changes in λ (300 K) as a function of fluence for LASL graphites irradiated in HT-29 have been reported[5] and are shown in Fig. B-2. For the graphite heat-treated at 2475 K, λ (300 K)* decreased from 80 W m^{-1} K^{-1} to about 15 W m^{-1} K^{-1} after 9.7 x 10^{21} n cm^{-2} at 1175 K. A pitch-injected fuel rod would be expected to have λ (300 K) of about 4 W m^{-1} K^{-1} after a similar irradiation. Before end of life (EOL), the value of $\lambda_{extruded}/\lambda_{pitch}$ is even more favorable.

*These measurements were made parallel to the extrusion axis. Perpendicular values are about 75% of these, before irradiation.

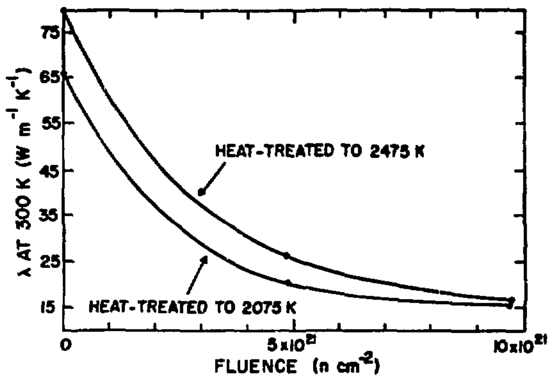

Fig. B-2.
Effect of irradiation on thermal conductivity of two LASL graphites (measurements made parallel to extrusion axis).

V. COMBINED EFFECT OF TEMPERATURE AND IRRADIATION

The total thermal conductivity in graphite is

$$\lambda = \lambda_e + \lambda_p,$$

where λ_e is the electronic component and λ_p is the phonon component of the heat transfer within the graphite. In well-graphitized, reasonably isotropic, polycrystalline, artificial graphites, λ_e, as calculated from the Wiedemann-Franz law, contributes about 2% of the total thermal conductivity. Although various theorists have estimated λ_e to be as high as 15% of λ, all agree that above room temperature it is the conduction of heat by phonons that is the important mechanism in graphite. The phonon component is given by

$$\lambda_p = \frac{1}{3} \sum_{i=1}^{n} c_i u_i \ell_i \ ,$$

where c_i is heat capacity, u_i is phonon velocity, and ℓ_i is the phonon mean free path, all for the ith acoustic mode. The phonon component, and thus λ, is a strong function of ℓ_i, and changes in λ may be considered in terms of changes in phonon mean free path. Effects of temperature on λ in graphite are readily interpreted in these terms, because above 350 K enough vibrational modes are excited that the phonons interact with each other and are scattered, thus decreasing ℓ. Solid state theory says that for phonon-phonon scattering,

$$\lambda \sim \ell \sim 1/T \ ,$$

and this is indeed the form of the graphite λ vs temperature curve from about 400 to 2500 K.

The effects of irradiation on thermal conductivity are analyzed in a similar manner. Graphite has a layered structure, and it is the phonons in the ab plane that are effective in heat transfer. Impurities, interstitials, or displaced atoms[6-8] are all effective in reducing the periodicity of the graphite lattice and acting as scattering centers. The dependence of the mean free path on defects in the lattice is generally taken to be

$$\ell \sim 1/c \ ,$$

where c is the concentration term of the defect involved. Thus, effects on the thermal conductivity due to T or to c may be similar.

Because both phenomena reduce the phonon mean free path, changes due to temperature and to irradiation are most pronounced in graphites with high degrees of crystalline perfection. Therefore, the extruded, highly crystalline, high-density fuel rods are more affected by temperature and irradiation than are the poorly graphitized fuel rods made by pitch injection. This also explains why irradiation has a larger effect on graphites heat-treated at 2475 K (and thus more fully graphitized) than those heat-treated at 2075 K (see Fig. B-2).

There is, however, an additional interaction of temperature with irradiation damage to the graphite; temperature anneals some of the damage. That is, the higher the irradiation temperature, the more any irradiation damage is annealed and the less irradiation affects λ. This is brought out very nicely in Price's article[8] about irradiation effects on λ of graphites irradiated in OG-2.[9]

One other effect must be noted. As thermal and irradiation effects degrade the crystalline perfection of the graphite lattice, further irradiation and thermal imperfections have a lessening influence. Thus if the graphite shown in Fig. B-2 had been irradiated at some higher temperature than 1175 K, the λ (300 K) would have been higher. Curves of λ (300 K) vs fluence in Price's article show that λ (300 K) > 50 W m^{-1} K^{-1} for all graphites irradiated at >1275 K and <50 W m^{-1} K^{-1} for those graphites irradiated at lower temperatures. Based on these considerations, it would be estimated that the λ advantage after an irradiation of 9.7 x 10^{21} n cm^{-2}, of the extruded fuels as compared to the pitch-injected fuels, would be considerably greater than a factor of 4 as the irradiation temperature was increased.

To summarize, irradiation has an adverse effect on λ; high-temperature operation decreases λ but ameliorates the irradiation damage effects. The higher the irradiation temperature, the less the overall effect.

VI. SUMMARY

- The fabrication of high-density, well-graphitized matrices containing 41-vol% coated particles has been demonstrated.
- At high temperature (1775 K) these matrices have a factor of 3-4 improvement in λ over the pitch-injected fuel rods at the same temperature.
- After irradiation at 1175 K, the value of λ (300 K) of the high-density matrix is estimated to have a thermal conductivity 3-4 times that of the pitch-injected fuel rods at EOL.
- The combined effects of high-temperature operation and irradiation on the high-density graphite matrix should result in a rod with a distinct heat-transfer advantage (>4 times) over the pitch-injected system. This should be true throughout the reactor operation lifetime with the minimum advantage occurring at EOL.

While the evidence has just started to come in on the performance of the high-density graphite fuel rods, all indications are that it is a system with demonstrable thermal performance advantages over the pitch-injected fuel rods.

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