UNCLASSIFIED

LA-5005

See Attached
Errata Sheet

ROVER DECLASSIFIED

C. 2

DO NOT CIRCULATE

Retention Copy

UNCLASSIFIED

Classification changed to
by authority of the U.S. ERDABy Michael W. Suits 5-19-77
(Signature of person making the change and date)

Development of Carbide-Carbon Composite Fuel Elements for Rover Reactors (U)

PUBLICLY RELEASABLE

Per E. M. Sandoval, FSS-16 Date: 7-12-88By Markus Lujan, CIC-14 Date: 10-26-95LOS ALAMOS NATIONAL LABORATORY
3 9338 00407 0065

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

AEC RESEARCH AND
DEVELOPMENT REPORTUNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

UNCLASSIFIED

CONFIDENTIAL

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Classified by John W. McDonald,
ISD-6 Classification Officer.

CONFIDENTIAL

OFFICE MEMORANDUM

TO : Holders of LA-5005

DATE: November 29, 1972

FROM : ISD-6

SUBJECT: Omission

SYMBOL :

On page 4 of LA-5005, the magnifications of the photomicrographs in Fig. 2 "Typical photomicrographs of Stark ZrC powder" were omitted. The upper photomicrograph was of the powder at 100X; the lower, at 250X.

UNCLASSIFIED

UNCLASSIFIED

ROVER - DECLASSIFIED

ISSUED: October 1972

Los Alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

Development of Carbide-Carbon Composite Fuel Elements for Rover Reactors (U)

by

K. V. Davidson—*Keith*
W. W. Martin—*Walter*
D. H. Schell—*Gerald*
J. M. Taub—*James*
J. W. Taylor—*Joseph*

LOS ALAMOS NATL LAB LIB
3 9338 00407 0065

AEC RESEARCH AND
DEVELOPMENT REPORT

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

UNCLASSIFIED

UNCLASSIFIED

DEVELOPMENT OF CARBIDE-CARBON COMPOSITE

FUEL ELEMENTS FOR ROVER REACTORS

by

K. V. Davidson, W. W. Martin, D. H. Schell, J. M. Taub, and J. W. Taylor

ABSTRACT

Nineteen-hole hexagonal fuel elements containing 30 vol% (U,Zr)C in graphite were successfully produced for the Rover reactor program. The elements were extruded from a mix consisting of graphite flour, carbon black, ZrC, UO_2 , and liquid thermosetting binder. Solid-solution (U,Zr)C was formed in the elements during heat treatment.

Parameters were developed for the extrusion and heat-treating operations. Specifications for raw materials evolved during the course of this program. An investigation of extrusion-die materials was undertaken, and Ferro-TiC was selected as the best material available at this time.

Techniques for brazing composite fuel elements to hot-pressed tips of refractory-metal carbide-graphite composite material and to other elements were developed.

INTRODUCTION

The cores of the reactors used in the Rover program have involved the same basic fuel-element design since the Kiwi-B4 reactor was fabricated in the early 1960's. The fuel elements are hexagonal in cross section, about $3/4$ in. across the flats, and approximately 52 in. long, and contain 19 longitudinal holes ranging in diameter from 0.093 to 0.102 in., depending upon the particular reactor design.

The fuel elements in the Kiwi-B4 reactor were extruded in the above geometry using a graphite extrusion mix loaded with the proper amount of enriched UO_2 .¹ During the high-temperature graphitizing operation, the UO_2 was converted to UC_2 , and the machined fuel element was then coated with NbC to protect the graphite from the hydrogen environment in the reactor. Problems originating with the bare UC_2 particles in the fuel element led to its replacement by a "bead," a dense UC_2 particle coated with 25 μm of pyrolytic carbon. The graphite matrix

was essentially unchanged and was subject to considerable carbon loss in a reactor wherever the NbC coating was cracked or missing.

While the fuel element improvements were under way, a development program was being pursued to obtain a hot-end support material less susceptible to damage in a hot hydrogen environment than the high-quality, coated graphite material then in use. A highly successful material emerged from this program, and it has been considered the "standard" hot-end support material for Rover reactors at both the Los Alamos Scientific Laboratory (LASL) and the Westinghouse Astronuclear Laboratory (WANL) for several years. This material is a hot-pressed composite of 46 vol% (TaC+NbC)-C, also known as 40TaC-40NbC-20C, by weight. One of the striking features of this material was that the chemical-vapor-deposited (CVD) coating of TaC or NbC could not be stripped from the composite except by grinding. The adherence of the coating to the matrix material was outstanding even after prolonged testing at high temperatures

UNCLASSIFIED

UNCLASSIFIED

in hydrogen. Another distinguishing feature of this matrix material was the integrity of the machined component even when all of the carbon had been leached out by hydrogen gas. There was enough continuous carbide matrix remaining so that the component retained its shape and did not disintegrate to powder in the hot hydrogen environment. These two outstanding support-material characteristics would be extremely desirable in a fuel element but, obviously, were not present in the bead-loaded, graphite fuel elements in use.

A limited development program was established to extrude a tubular graphite shape containing NbC particles whose NbC content ranged from 0 to 40 vol%.² The program was to determine the effect of carbide content on the properties of the extruded composite tubes. As expected, most of the properties increased with increasing carbide content. Of greater interest, however, was the fact that shapes containing relatively large amounts of carbide particles could be extruded successfully.

Another development program then was initiated to evaluate the possibility of making a hexagonal 19-hole fuel-element extrusion in which the uranium fuel would be an alloy of UC-ZrC and the total carbide loading would be high enough to form a carbide network like that in the support material described above. Uranium dicarbide is very reactive and could not be used for this purpose. We knew from materials developments in other IASL programs that a solid-solution particle of UC and ZrC was not reactive under normal conditions, particularly if the uranium content remained below 18 mole % where there should be no free UC₂ present to hydrolyze. Fortunately, the uranium loadings anticipated for a Rover reactor generally would fall below this 18 mole % maximum.

There are several ways to arrive at a (U,Zr)C-C composite. Solid-solution (U,Zr)C powder could be made separately and added to a graphite extrusion mix, but this would have been quite difficult considering the existing state of the art for making (U,Zr)C particles. The best approach at the time was to make UO₂ and ZrC powder additions to the graphite extrusion mix, and to let the (U,Zr)C solid solution form in situ during heat treating of the extruded shapes.

The total volume percent of carbide loading (UC+ZrC) was dictated by the properties of the

elements. If the loading were too low, the element would not have a continuous carbide network and would have little integrity if the free carbon were lost. If it were too high, the element would have undesirable thermal stress characteristics. The first experiments produced a 50 vol% carbide composite fuel element, but the thermal-stress evaluation was so unfavorable that we decided to approach the carbide level by working up from a low level. We prepared 20 and 25 vol% carbide fuel elements, but most of the work described herein involved 30 vol% of carbide. This material has both a continuous carbide and a graphite structure.

The composite material is very abrasive, making it more difficult to machine than graphite fuel elements. The outside hexagonal surface could be milled using diamond-tipped cup wheels. This was not a difficult operation, being similar to that used for machining graphite elements. The diamond tools lasted a reasonable length of time, in that 100 elements could be machined before adjustments to compensate for wear were required.

Reaming the holes was an entirely different matter. A tungsten carbide-tipped reamer would ream 100 or more holes in graphite elements but was badly dulled by reaming one hole in a composite element. Using a dull reamer causes the outside or thinnest wall of the hole to break. Reaming the holes was not impossible, but appeared to be impractical for a production operation.

For the most part, the hole diameters in graphite fuel elements were within ± 0.001 in. of a nominal diameter. If we could obtain the same tolerance with the composite elements, we would not have to ream the holes. Some leeway in hole size is permissible because the gas flow through the fuel element is actually controlled by orifices at the inlet end of the element. Experience showed that the hole size of heat-treated composite elements could be controlled so that reaming was not necessary.

The 19 holes in a fuel-element cross section must be positioned accurately so that the web thicknesses between the holes and between the 12 outside holes and the outside of the element do not vary appreciably. The tolerance placed on hole location was ± 0.006 in. of the specified position. This was achieved for most composite fuel elements. If the web thicknesses vary, the amount of fuel in the

UNCLASSIFIED

UNCLASSIFIED

webs varies and the temperatures will not be uniform. A thick web not only generates more heat than a thin web, it makes the heat path to the coolant longer, thus accentuating the problem. If some webs in the cross section of an element are thicker than desired, then others are thinner. The resulting thermal gradients produce abnormal stresses within the element.

MATERIALS

Zirconium Carbide

Zirconium carbide from two producers was used in this program. Most of the work utilized reactor-grade ZrC (< 200 ppm Hf) powder purchased from Hermann C. Stark of West Germany. This powder was 88.3% zirconium and 11.5% total carbon of which $\sim 0.2\%$ was free carbon. Impurities included 0.2% N_2 , 0.2% O_2 , and 90 ppm of sulfur. Metallic impurities were very low, the major ones being 200 ppm of titanium, 150 ppm of tantalum, and 100 ppm of iron. Typical properties for this high-density, nonporous ZrC powder were determined at LASL and were as follows: bulk density, 2.45 g/cm^3 ; tap density, 3.78 g/cm^3 ; pycnometer density, 6.6 g/cm^3 (98.1% of theoretical); Fisher average particle size, $3.35 \mu\text{m}$; Fisher porosity, 0.469; and Numec surface area, $0.951 \text{ m}^2/\text{g}$. A typical Sedibal particle size-distribution curve is shown in Fig. 1, and photomicrographs of the ZrC powder are shown in Fig. 2. Zirconium carbide powder purchased from Kawecki Berylco, Inc., New York, NY was used in limited amounts. Except for much higher sulfur and oxygen contents, 0.5% and 0.7%, respectively, it was essentially the same as the material purchased from Stark.

The large lots of ZrC powder were received in pails each containing 100 lb. There was very little variation from pail to pail and, in most cases, from shipment to shipment for a particular powder lot. However, to ensure a uniform supply for numerous experiments and production, we cross-blended 20 to 24 pails of the powder. The ZrC powder was transferred from the pails into four polyethylene-lined 55-gal drums through use of a four-way splitter. The drums were rolled to homogenize the powder, and the powder was screened through a 200-mesh sieve before use.

Uranium Dioxide

The depleted UO_2 powder used in all development work was standard densified oxide made by LASL Group

Fig. 1. Typical Sedibal curve for ZrC powder.

CMB-8. This material is -325 mesh and has an average particle size of 4 to 5 μm .

The enriched UO_2 powder used in the fuel-element extrusion mix was also made by Group CMB-8 and was similar to the depleted oxide. The specification called for a powder having a Fisher average particle size of $5 \pm 0.25 \mu\text{m}$, a bulk density of 3.8 g/cm^3 or higher, a tap density of 5.5 g/cm^3 or higher, and a minimum total uranium content of 87.5%. The total metallic impurities were limited to 500 ppm, with a maximum of 1 ppm of boron and 0.5 ppm of cadmium. A typical Sedibal particle-size distribution curve for UO_2 is shown in Fig. 3.

At one stage of fuel-element production, we used UO_2 that contained a greater percentage of fines ($< 2\text{-}\mu\text{m}$ particles) than normal and only 10 to 15% of whose particles were larger than 10 μm . This powder tended to agglomerate because of the large quantity of fines and formed areas of high uranium concentration in the elements. Once the problem was recognized, Group CMB-8 was able to produce UO_2 powders with a more normal particle-size distribution.

See Attached Fig. 2. Typical photomicrographs of Stark ZrC
Errata Sheet powder.

Graphite Flours and Carbon Black

The main graphite flour used in this program was grade S97 flour obtained from Speer Carbon Company, St. Mary's, PA. The particle-size distribution as determined by sieve analysis was 2% -65 +200 mesh, 8% -200 +270 mesh, 20% -270 +325 mesh, and 70% -325 mesh. This S97 flour was a high-purity graphite containing 100 ppm of ash, and it had a Fisher average particle size of 4.75 μm .

We had to use a finer graphite flour for the composite extrusions than for bead-loaded extrusions. The type 1008S graphite flour used in the bead-loaded fuel elements was all -60 mesh, 42% -60 +200 mesh, 25% -200 +325 mesh, and 33% -325 mesh, and was very satisfactory for these extrusions. However, in the composite extrusions where an appreciable amount of the dry ingredients are 3- to 5- μm powders, the large graphite particles such as those in the 1008S flour formed unloaded islands that were surrounded by a relatively high concentration of carbide. This tended

to give the extrusion a carbide matrix and, therefore, the properties of a carbide extrusion. The net result was an element with low thermal stress resistance. When made from the finer S97 graphite flour, the carbide structure was still continuous but finer, so that, for a specific volume percent of loading, we obtained an element with improved thermal stress resistance. If we used a very fine graphite flour ($< 1 \mu\text{m}$) in the extrusion, extrusion flaws and cracks and spalls occurred during heat treatment. The S97 particle distribution was a compromise in this respect, but it was commercially available.

The S97 flour was received in 55-gal drums, each containing ~ 300 lb. We rolled the drums to eliminate segregation that might have occurred during shipping, and sampled each for radiographic examination to detect high-density impurities.

The flour from eight drums that had passed radiographic evaluation was cross-blended into nine drums. The cross-blended flour was screened through a 60-mesh screen using an Abbe 2 Turbo Sifter. The tailings were passed through the sifter three additional times for a net recovery of 98 to 99%. The flour discharged from the sifter passed through an Eriez

Fig. 3. Typical Sedibal curve for UO_2 powder.

UNCLASSIFIED

cles. The flour was collected in clean 55-gal drums, and each drum was then rolled at 40 rpm for 8 h to homogenize its contents. The contents of each drum was sampled for screen and chemical analysis and radiography.

Thermax is a carbon black obtained from the Thermatomic Carbon Company, Sterlington, LA. It has a Fisher average particle size of $< 1 \mu\text{m}$, but when examined microscopically it is seen to consist of roughly spherical particles about $0.3 \mu\text{m}$ in diameter. Thermax is relatively impure, containing up to 4000 ppm of ash, mostly silicon.

The Thermax was received in paper bags each containing 50 lb. The Thermax from four bags was placed in a 55-gal drum, screened through a 60-mesh screen, and passed through a magnetic grate. The screening was to break up Thermax agglomerates. The drum of screened Thermax was not rolled because that would form more spherical agglomerates. The contents of each drum was sampled for chemical analysis and radiography.

The proper quantities of graphite flour and Thermax required to make a 100-kg batch, usually 85 parts flour to 15 parts Thermax, were weighed and placed in a 55-gal drum. This drum contained a baffle of expanded metal to facilitate mixing and was rolled at 40 rpm for 8 h. Again, a sample was taken for radiography and chemistry.

Binder

We used Varcum 8251 thermosetting resin as the binder in all extrusions. Varcum is a partially polymerized furfuryl alcohol having a viscosity of about 300 centipoises at room temperature. It is a product of the Varcum Chemical Division of Reichhold Chemicals, Inc.

The drums of Varcum were cross-blended by the manufacturer, and the resin was shipped in 55-gal drums. After receipt at IASL, it was stored in a cold room at 15°C before use. When a drum of Varcum was to be used, it was rolled on a barrel roller for 1 h and the contents was transferred to 5-gal cans. These cans were then taken to the mixing area as required.

The Varcum was catalyzed with 4 g of maleic anhydride per 100 cm^3 of resin. The maleic anhydride was ground and screened to -20 mesh before use. The resin-catalyst mixture was placed in a 1-gal

min before use. The catalyst, in this amount, was slow in acting at 40°C , so processing times were not sensitive. The composite mixtures were usable after several days of storage at room temperature and after several weeks of storage at 2°C .

PROCESSING

Mixing

All small development batches, usually calculated to produce 100 or 200 cm^3 of the final product, were mixed by hand. The dry ingredients were weighed and placed in a glass jar containing aluminum wires to enhance mixing. The jar was placed on a roller and rolled for $1/2 \text{ h}$. The blended material was then placed in an evaporating dish, and the catalyzed Varcum was hand-mixed with the dry ingredients.

Large batches, enough to make 2000 to 3000 cm^3 of final product, were mixed in Patterson-Kelly (P-K) 16-qt twin-shell blenders. The blenders were equipped with an intensifier bar and liquid addition apparatus used to mix dry ingredients and to blend dry ingredients with the liquid binder. The dry ingredients were weighed, placed in the blender, and dry blended for 5 min with the intensifier bar rotating at 900 rpm. Catalyzed Varcum was weighed and placed in a heated (40°C) reservoir that had a tube leading to the liquid addition apparatus of the P-K blender. The reservoir was pressurized with air at 1-3 psi, and the Varcum was added to the blender over a period of about 15 min. The blender was opened, and its walls and lids were scraped free of adhering material. It was then closed, and blending was continued for an additional 5 min using the intensifier bar. The material blended one day was normally not extruded until the next. This aging of the mix was not necessary, but it did seem to make the mixes more uniform during extrusion and was done also to conserve man power. A person who mixed one day could extrude the next.

Just before being extruded, the larger batches were mixed intensively by passing them through a Hobart Model 4532 2-hp meat chopper made by the Hobart Manufacturing Company, Troy, OH. We used a breaker plate with $3/16\text{-in.}$ -diam holes for this work. This operation was used to homogenize, densify, and heat the extrusion mix. The mix was usually passed through the chopper twice before extrusion and once between each extrusion.

UNCLASSIFIED

The ~100 cm³ batches were too small to be ground in the meat chopper. These mixes, especially the highly loaded ones, were often first extruded through a relatively large, simple die to further mix the material before making the final extrusion.

Extrusion

We extruded small experimental batches using a LASL-made, 24-ton horizontal hydraulic extrusion press having either a 2- or 2.5-in.-diam extrusion chamber. Shapes up to 1/2 in. in diameter were extruded on this press. We extruded larger batches for larger pieces using either a LASL-made, 100-ton or an Elmes 150-ton press each of which had a 6-in.-diam extrusion chamber.

All presses were equipped with variable-volume hydraulic pumps that allowed the extrusion speed to be varied widely. Once an extrusion speed was set, extrusions were made at a constant rate regardless of minor variations in the extrusion pressure. All presses were also equipped with vacuum systems for evacuation of the extrusion die, chamber, and mix before and during extrusion. Air trapped in the extrusions causes serious blistering. The volatiles from the mix were kept from the vacuum pumps by liquid N₂-cooled cold traps. We had to pull a vacuum of less than 1 mm Hg on the mix before extrusion; otherwise, the cured extrusions would contain blisters, spalls, or other flaws.

The die used for making 19-hole composite extrusions was the product of an extensive development effort spanning several years. There were two pin holders; one for the center pin and one for the other 18 pins. The pin pattern (spacing between pins) was changed slightly from that used previously for bead-loaded graphite, to accommodate the greater shrinkage of the composite material during heat treatment. The plenum generated the hexagonal outer geometry of the fuel element. We increased the size of the corner cut-outs, and machined a small (shallow) inlet angle on the flat surfaces of the plenum to facilitate flow of the extrusion mix. Adding this inlet angle to the plenum resulted in satisfactory extrusions. This angle, affecting the direction of flow of the extrusion mix, does move the outer holes toward the center somewhat and must be taken into account when determining the die-pin locations. Figures 4 and 5 show 19-hole and small 1-hole extrusion tooling components, respectively.

Fig. 4. Extrusion tooling for 19-hole hexagonal fuel elements.

Extrusion pressures varied widely, but good mixes usually could be extruded at 3000 to 4000 psi. Some soft mixes extruded at 1000 psi, but they usually did not produce very good pieces. Other mixes would extrude at the pressure limit of the presses, about 10,000 psi for the 150-ton press and 15,000 psi for the small 24-ton laboratory press. The viscosity of the composite mix was controlled mainly by the Varcum binder content. The extrusion pressure was controlled both by the viscosity of the mix and by the extrusion speed.

The extrusion speed varied considerably, but it was seldom more than the 20 ft/min used for both fueled and unfueled graphite extrusions. In general, small simple shapes were extruded at around 15 ft/min, whereas the rate for 19-hole extrusions usually varied from 2 to 5 ft/min. The extrusion speed was kept as high as possible, within practical limits, but was usually quite slow because of cracking problems. In general, if an extrusion cracked as it emerged from the die, we decreased the extrusion speed and this often corrected the problem. If it seemed that the die was not filling properly, as

Fig. 5. Extrusion tooling for cylindrical extrusions.

UNCLASSIFIED

UNCLASSIFIED

shown by bad cracks over a corner hole, we would increase the speed considerably for a few seconds to try to clear the feed holes in the die and then decrease it to the desired speed.

When possible, production elements were extruded at a rate of one element length (63 in.) in 90 sec, or approximately 0.7 in./sec. This seemed to be a practical speed that produced high-quality elements. Experiments indicated that extruding too fast produced elements with lower densities and higher permeabilities. Extruding very slowly produced satisfactory elements, but it was not practical for a production operation.

As mentioned, extrusion quality was of primary importance and, when necessary, we adjusted the extrusion speed to produce crack-free elements. At the start of the 19-hole composite extrusion program, we used the same die that had been used for making graphite elements. Extrusion-speed adjustments alone did not provide satisfactory elements because the friction characteristics of the composite material were quite different from those of a graphite extrusion mix. Minor die changes (larger corner cutouts and a tapered plenum inlet) plus speed adjustments and minor adjustments to the extrusion mix were required. As raw materials and element compositions change, further die modifications may be necessary.

THERMAL PROCESSING

Curing

We cured the extrusions, i.e., polymerized the thermosetting resin binder, in electrically heated circulating-air ovens, Model FO 962430, made by the Cooley Electric Manufacturing Corporation. A cam-operated Wheelco controller provided the desired heating cycle. The normal cure was to a temperature of 250°C. We used two different heating cycles with heating times of 63 and 93 h, respectively. Thin-walled shapes, or development extrusions whose quality was not critical, were cured using the 63-h cycle. Thick-walled shapes and actual fuel elements were cured on the longer cycle. The long curing times were essential because polymerization of the binder resin produced a considerable volume of gas. Heating the elements too rapidly at this point would build up internal gas pressure and crack the weak fuel-element structure.

The heating rate for the 63-h cycle was 3°/h from 45 to 90°C, 1°/h from 90 to 110°C, 2°/h from 110 to 130°C, and a gradual increase to a maximum of 8°/h from 130 to 250°C. The heating rate for the 93-h cycle was 1°/h from 50 to 110°C and the same as the 63-h cycle from 110 to 250°C.

Extrusions were always cured in a horizontal position. All extrusions except heavy ones requiring the air-vein fixture (described later) were cured in the graphite fixtures into which they were extruded. Fuel elements extruded into the air-vein fixture were cured in individual fixtures. The ends of all fixtures where the pieces were exposed to the oven atmosphere were wrapped with aluminum foil. We did not try to actually seal the fixtures. After curing, it was important not to remove the cured extrusions from the fixtures until the fixtures had cooled almost to room temperature; otherwise, the extrusions were apt to warp.

450°C Heat Treatment

All cured extrusions except small shapes made for development purposes were heat treated to approximately 450°C before being baked. For this heat treatment, we placed the extrusions in layered hexagonal graphite fixtures that were placed in a stainless steel can kept under a slight positive pressure of N₂ to prevent oxidation. This can was placed in the same type of circulating-air oven used in the curing operation. The heating cycle from 200 to 450°C (oven temperature) took 63 h at a rate of 3-1/3°/h after an initial 3-h heating to bring the oven temperature up to 250°C. After the 450°C heat treatment, the extrusions were furnace cooled essentially to room temperature before being removed from the fixtures.

Baking

The baking of composite extrusions consisted of heating them to 850°C in a soft vacuum using a helium or argon flush through the furnace. The pressure in the baking furnaces, using the vacuum pumps alone, was not low enough to prevent oxidation of the ZrC in the extrusions. The products of decomposition of the Varcum binder, especially the water vapor, were sufficiently corrosive to the ZrC at the baking temperature to produce considerable loose ZrO₂ powder on the surfaces of the extrusions. An adequate supply of inert gas flowing through the 19 holes and around the outside of the extrusions

UNCLASSIFIED

UNCLASSIFIED

diluted and swept these products away, thus considerably reducing the surface oxidation.

We used a horizontal baking furnace, Model T 1515-140, manufactured by the L&L Special Furnace Co., Upland, PA., for early development work. This furnace has a maximum temperature capability of 950°C and a 3.75-in.-i.d. by 8.0-ft-long heated work zone. A model KC-46 mechanical vacuum pump, manufactured by the Kinney Vacuum Corp., New York, NY, maintained pressures of 0.1 to 1.0 torr, depending upon the rate of gas evolution and/or the rate of introduction of inert gas. A liquid-nitrogen cold trap protected the pump from the binder decomposition products.

The production type of baking furnace was designed and built at IASL when graphite fuel elements were being produced. This is a vertical furnace heated by two-zone resistance heating elements each controlled by cam-operated Wheelco controllers. The hot zone of the furnace was 16 in. in diameter and 60 in. long; the furnace normally operated under a pressure of 10 torr or less. The vacuum system for a furnace used for development and hardware production consisted of a two-stage Nash Hytor pump: two Model TS-10 pumps connected in series but powered by a single 10-hp electric motor. A triple-stage steam ejector provided the vacuum on the three available production furnaces. An air-operated valve in the vacuum line prevented air from being drawn into the furnace through the vacuum pump in event of a power or steam failure. Also, a self-opening trap prevented water from the vacuum pump from entering the furnace.

It was impractical to use mechanical pumps to evacuate the large baking furnaces because of the large amount of tarry material released by the Vacuum. Previous experience had demonstrated rapid fouling of the pumps.

In the production furnaces, the extrusions were placed vertically in graphite fixtures. Inert helium or argon gas was introduced into the top of the furnace through a pipe that ran down one of the holes in the fixture to a stainless steel distribution plate. We tried to make the plate fit snugly on the bottom of the fixture so the gas would not leak out. The plate distributed the gas uniformly to the bottom of each hole in the fixture where the gas was free to flow upward, helped by the vacuum, through and

around the extrusions. Hexagonal extrusions were baked in fixtures that had round holes to allow the inert gas to sweep past the outside surfaces of the elements. The gas flow was about $3/4$ ft³/h/extrusion.

Extrusions previously heat-treated to 450°C were baked for 39 h to 850°C. After an initial 3-h heating to bring furnace temperature up to 450°C, the heating rate was 5°/h for 6 h, then 8.33°/h for the rest of the run.

Extrusions cured to 250°C only and not heat-treated to 450°C were baked for 48 h. An initial 3-h heating brought the furnace temperature up to 250°C. The heating rate from 250 to 610°C was 10°/h, and that from 610 to 850°C was 25°/h.

High-Temperature Heat Treating

Composite elements and hardware extrusions were high-temperature heat treated in induction-heated vertical furnaces designed and built at IASL. The induction coil was powered by a 175-kW, 960-cycle, motor-generator set. The 82-in.-long coil consisted of 6-in.-wide flat copper strips, roll-formed and silver-soldered together to form a cylinder. Three parallel copper tubes to carry cooling water were silver-soldered to the outside of the coil as shown in Fig. 6. Note that the furnaces were originally designed to heat graphite fuel elements to a nominal temperature of 2200°C or less.

Three furnaces that had temperature capabilities of 2500°C in the axial center of the fixture were available. Two were later modified to allow processing of composite elements to 2700°C at their axial centers. Figure 7 shows these two furnaces.

The unmodified furnace is used primarily to heat treat hardware and miscellaneous extrusions. It will accommodate a fixture containing up to 90 fuel-element-size pieces. The fixture is located within an 18.75-in.-o.d., 16.50-in.-i.d. graphite susceptor. The susceptor, in turn, is surrounded by a 3-in.-thick layer of carbon-black insulation, a 1-in.-thick ceramic liner, a layer of Fiberfrax, a 0.010-in.-thick mica sheet, and the induction coil.

The furnaces modified to go to a higher temperature are the same as that above except that the outside diameter of the susceptors was decreased to allow for an increased thickness of carbon-black insulation. The fixture is 13-3/8 in. in diam and will hold up to 71 fuel elements.

UNCLASSIFIED

UNCLASSIFIED

Fig. 6. High-temperature furnace induction coil.

Fig. 7. High-temperature heat-treating furnaces.

These two furnaces were used to heat treat all fuel elements, both low fired (2350°C) and high fired up to 2700°C .

The temperature in the furnaces was measured optically through a sight port at the top that sighted into a hole in the graphite fixture. A helium or argon flush kept the sight port clear of smoke and prevented the graphite in the furnace from oxidizing.

The graphite fixture that held the baked elements for the first high-temperature heat treatment (2350°C) had hexagonal holes designed to keep the elements from twisting. The heating rate for the first high-temperature heat treatment varied somewhat during its development, but now is as follows: 2-1/2 h to 1600°C , a 3-h drift upward to 2350°C at reduced power, and a 2- to 6-h hold at 2350°C .

During the slower-rate heating, the UO_2 in the extrusions reacted with the carbon surrounding the particle and was converted to the dicarbide with the evolution of CO gas. The slower heating rate was intended to accommodate release of this gas without injuring the element. Subsequent heating promotes formation of the (U,Zr)C solid solution. The hold at 2350°C was to allow complete solid-solution formation below the UC_2 -C eutectic melting temperature (2410°C). X-ray diffraction of elements heat treated under these conditions almost always showed that the uranium and zirconium were present as single-phase solid solution.

The graphite fixture that held the elements for the second high-temperature heat treatment also had hexagonal holes. The holes were smaller than those in the previous fixture to compensate for the fuel-element shrinkage encountered during low fire and to provide a tight fit for the low-fired elements. The baked elements shrink about 2% across the flats during the first high-temperature heat treatment and shrink an additional 0.5% during the second treatment. The heating rate for the second treatment was 3 h to 2350°C with a 1-h hold at temperature. The temperature was then increased to the desired point, depending upon the uranium loading, and the fixture was held at temperature for 2 h. The maximum temperature was 2700°C .

There were several reasons for the double high-temperature heat treatments. The time required for formation of the solid solution (U,Zr)C is such that

UNCLASSIFIED

a single treatment to the final temperature could not be completed in a normal 8 to 5 work day. Also, it is very important to keep the elements as straight as possible so that they will pass through the shop machining operations without breaking. This was accomplished by placing elements from the first heat treatment into tighter fitting fixtures for the second heat treatment and splitting the total shrinkage so that most of it occurred during the first treatment. This means that after the second treatment the elements are contained quite tightly in the fixture. Composite elements will bow as much as they are allowed to by the clearance in the fixture. The ends of an element, especially that upon which the element rests, tend to bow or "hook" in the last few inches. If this bow is excessive, over 15 mils, the element cannot be fed through the milling machines without breaking. Bowing also tends to displace the hole location of a milled element.

The high-temperature heat-treating furnaces originally were designed to operate at about 2200°C for the manufacture of bead-loaded graphite elements. With the insulation modification mentioned previously, the operating temperature was raised to 2700°C. However, this was accomplished only with considerable sacrifice in temperature uniformity within the furnaces. There are no provisions in the power input into the furnaces to compensate for the large heat losses at their ends. Therefore, when the axial center of a 56-in.-long fixture is at 2700°C, the bottom is at approximately 2450°C, and the top is at about 2550°C. Therefore, the element does not shrink uniformly. Besides creating differences in dimensions across the flats of the element, the nonuniformity affects the hole size, hole location, uranium loading (g/cm^3), and volume percent of loading. A high-temperature furnace with three or more heating zones that can be controlled independently to level out the temperature profile has been designed and is under construction.

DISCUSSION

Several hundred carbide-graphite composite fuel elements and hardware pieces were extruded and processed through the heat-treating cycles. Before making a large number of fuel elements, we made several development lots to gain experience in handling the composite material and to provide pieces that

could be processed through the entire fuel-element "pipeline." As is usual when starting a development program such as this, we encountered several minor difficulties. The early composite work was based on graphite technology developed and evolved over a period of several years. Many procedures and techniques and most of the equipment used on the graphite work were used for making the composite fuel elements.

Some of the problems encountered in making composite fuel elements have been mentioned or discussed previously. We will now discuss them in more detail.

Raw Materials

The previously noted problem of the UO_2 particle size was corrected by minimizing the amount of fines ($< 2 \mu\text{m}$ particle size) to eliminate the agglomeration during blending and mixing. The ZrC powder was quite satisfactory except for the material containing 5000 ppm of sulfur as an impurity. This particular material yielded low-density, highly permeable, weak fuel elements, generally inferior to other elements made with ZrC of low sulfur content. A maximum of 500 ppm of sulfur was considered acceptable, and this fact was added to the LASL specifications for ZrC powder.

Extrusion Tooling

One of the main problems in extrusion of composite materials was wear of the extrusion tooling. The carbide and oxide particles in the mix, especially the ZrC particles, tend to be angular and are very hard and make the mix very abrasive. Die wear is particularly severe where the flow of extrudate impinges on a die surface and changes direction, as on the upstream face of the plenum and at the bases of the pins. This was particularly evident on the outside row of pins. Surfaces over which the mix slides are also worn, but to a lesser degree. These surfaces include the extrusion cylinder, ram head, feed holes, pin diameters, and the plenum near its exit end. After much experimentation, we chose Ferro-Tic C, a steel-bonded carbide manufactured by Sintercast, West Nyack, NY, for its ease of fabrication and very high wear resistance. Hardnesses of R_c 68-71 are obtained in the heat-treated condition.

Die wear is a serious problem for several reasons. The composite materials do not machine

UNCLASSIFIED

readily, so we do not ream the holes in the fuel elements. The die pins are sized so that after an element has been heat treated the holes are of the desired size, usually 0.102 in. in diameter. This size should be maintained to ± 0.001 in. Pin wear would have obvious consequences.

Plenum wear causes a variety of problems. Wear on the inlet end changes the filling characteristics of the die and could cause cracked extrusions. Wear further toward the exit changes the hole location in the extrusion because the 18 pins, especially the outer 12 are pushed inward. In fuel elements, the location tolerance for each of the 19 holes is 0.006 in. Plenum wear at the exit end produces over-size extrusions that may cause trouble when being fitted into the various fixtures for heat treatment. The net result of plenum wear probably affects the mechanical properties of a finished element, including its porosity.

The affects of die wear noted above were considered quite serious with respect to the problem of producing large numbers of uniform fuel elements for a reactor. Consequently, we planned a so-called "die-wear" experiment to evaluate other extrusion-die materials in an attempt to find a material or coating that would resist abrasion better than the hardened D-3 steel dies used for extrusion of graphite fuel elements.

Die-Wear Experiment

We designed an experiment that used a nozzle insert and an interchangeable pin in a die setup for 1/4-in.-o.d. by 0.1-in.-i.d. tubular extrusions. This die was used in the 24-ton horizontal extrusion press with a 2-in.-diam extrusion cylinder.

We selected a number of materials for evaluation, mainly high-wear-resistance tool steels, ceramics, and carbides for the nozzle inserts, and tool steels and coated steel for the pins. We measured the inside diameters of the inserts at the inlet and exit ends. We measured the insert length also so that we could detect wear on the flat upstream surface. The pin diameters were measured at two points, where the extrudate coming through the annulus between the spider and the nozzle insert impinged on the pin, and at the exit end of the pin.

The experimental procedure was to extrude a certain amount of abrasive material through the die and pin combinations and then measure changes in

die and pin dimensions. The same mix, speed, and temperature conditions were followed for each set of inserts and pins. An insert and pin were tested at the same time although they might have been made from different materials. The extrusion speed was controlled by the setting of the variable-volume hydraulic pump on the extrusion press. These settings followed the same pattern for each extrusion batch. The extrusion speeds and pressures did vary somewhat. Some of this was a batch-to-batch variation that may have been caused by the friction characteristics of the insert or pin. Some was the normal decrease in extrusion pressure as a batch is extruded a number of times, followed by increased pressure during further extrusions as the batch dries out partly because of loss of binder owing to the vacuum applied before each extrusion.

We gave considerable thought to the abrasive mix that was to be extruded. A fairly large quantity (100 lb) of a cheap abrasive was required. We found an Al_2O_3 powder (Norton 38-900) that had an average particle size of 2.1 μm , in the range of the oxide and carbide particles being used in fuel-element extrusions. Also, the particle shape was angular, like that of the oxide and carbide powders being used.

The extrusion mix consisted of 66.7 g of S97 graphite flour mix, 400 g of Al_2O_3 , and 102.9 g of Varcum binder. This approximates 50 vol% of the abrasive in the mix. We blended the dry ingredients together for 1/2 h, and mixed the liquid Varcum with them by hand. The mix was extruded eight times through the die being tested. This mix was then discarded, and a new mix was made and also extruded eight times. This constituted one die test with a total extrudate length of approximately 320 ft.

We tested nine die setups in this manner. The spider that holds the pin in place was new at the start of these experiments. This new spider required that after the extrudate passed through the spider it pass through a 1/16-in.-thick annulus created by the bottom of the spider and the top of the insert. The result was that the bottom of the spider wore so that the annulus height increased. So, as the experiment progressed, the severity of the test decreased in relation to the wear on the top of the insert and the base of the pin. After the nine die setups were tested, the spider was so

badly worn that part of the pin which was normally inside the spider was exposed to the flowing extrudate. In some cases this didn't make much difference, but the coating of coated pins now ended where the pin normally was covered by the spider, so that uncoated metal was exposed.

To try to compensate the decreasing severity of the test resulting from wear on the various setups, we tested the nine setups again but in reverse order. This meant that at the end of the test each die setup had been used to extrude four abrasive batches each of which was extruded eight times, for a total of approximately 640 ft of extrudate. The bottom of the spider was now worn back as much as 47 mils from its original surface, and the cone-shaped protrusion in the center of the bottom (downstream) side of the spider which helped hold the pin was worn back 76 mils from its original surface. The feed holes through the spider increased in diameter about 7 mils.

The materials tested in the die-wear experiment and the data obtained are shown in Table I. The materials are listed in the order in which they were first tested. The numbers reported are the results after the completed experiment, two tests on each die setup, and indicate the changes in dimension occurring at the positions shown in Fig. 8.

Fig. 8. Positions of die-wear measurements.

As a result of these experiments, we purchased Ferro-Tic Grade-C stock and made all production dies and some development dies from this material. It is apparently no more difficult for the shop to machine the Ferro-Tic than the D3 steel, and the Ferro-Tic tends to be more stable during heat treatment. The main disadvantage is that Ferro-Tic has low ductility, and pin breakage has increased. The center pin in the 19-hole extrusion tooling or a single pin in a

TABLE I
CHANGES IN TOOLING DIMENSIONS DUE TO WEAR

Material	Change (Mils) Location, see Fig. 8				
	A	B	C	D	E
AISI-D3 Stl. RC-62	8.6	1.9	14.1	3.7	2.0
AISI-O2 Stl., Urethane Coated	25.9 ^a	4.0	21.1 ^a	10.2 ^a	9.0 ^a
Chromewear Stl. RC-65	3.4	0.4	11.4	0.5	0.5
Ferro-TiC Grade C. RC-70	0.2	0.4	0.8	0.3	0.1
Vasco Supreme Stl. RC-65	3.4	0.2	1.7	0.5	0.1
Zircoc 1027 (Insert only)			4.3	0.3	0.6
Al ₂ O ₃ 995 (Insert only)			0.5	0.5	0.1
Al ₂ O ₃ 8 (Insert only)			0.6	0.2	0.2
NbC, Hot-Pressed (Insert only)			1.0	0.4	0.2
AISI-M2 Stl. Metco 32C Coat (Pin only)		0.9	0.0		
AISI-M2 Stl. Metco 15E Coat (Pin only)		15.8 ^a	2.8		
AISI-M2 Stl. Metco 101 Coat (Pin only)		10.9 ^a	10.4 ^a		
AISI-M2 Stl. Metco XP-1122 (Pin only)		2.0	Chipped		

^a 4 to 6 mil-thick coating completely removed.

UNCLASSIFIED

UNCLASSIFIED

1-hole setup is especially susceptible to breakage during die disassembly. The actual experience with Ferro-Tic in extruding composite fuel elements has been very good.

Fuel-Element Taper

Composite extrusions highly loaded with ZrC or (U,Zr)C are heavy, as well as soft and rubbery before curing, and tend to deform. Extrusions as they emerge from the extrusion die normally slide along a contoured groove in a graphite curing fixture. The extrusion naturally encounters some sliding friction which apparently is not enough to deform an unloaded or lightly loaded extrusion. However, because of the softness and higher density of the highly loaded composite extrusions, the increased friction between the fuel element and the fixture caused a relatively uniform taper in the extrusions which was maintained throughout the heat treatments.

The first material emerging from the extrusion die, the "H" end of an element, was small or had "normal" dimensions across the flats. The extrusion became progressively larger so that the last material emerging from the die, the "G" end of the element, was several mils larger across the flats than the first material.

The amount of taper varied from batch to batch but was often 0.3 to 0.5 mils/in. Therefore, we made many of the early extrusions in short lengths so that the large ends would still fit into the grooves in existing heat-treating fixtures. We tried various means to reduce the sliding friction such as using Teflon and silicone sprays and polishing the graphite fixtures. Polishing the fixtures reduced the taper somewhat, but the results were not consistent.

To overcome this problem of tapered fuel elements, we designed extrusion fixtures with a row of small holes in the bottom of the appropriate groove, through which air was blown. These fixtures provided an air cushion for the extrusion and appeared to work quite well in that the dimensions of extrusions varied only a few mils along the extrusion, from flat to flat, from piece to piece, and from batch to batch. The nonuniformity in an extrusion made using this "air vein" fixture was generally not a taper, but random variations. All highly loaded extrusions made since May 1967 were made using this fixture, shown in Fig. 9.

Fig. 9. "Air-vein" extrusion fixture.

The larger extrusions were not cured in the air-vein fixture, but were transferred to individual graphite curing fixtures. After a piece was extruded, the bottom half of a curing fixture was placed on top of it in the air-vein fixture. This assembly was then turned over, and the air vein was removed, leaving the extrusion in the graphite curing fixture. A graphite top was then placed over the extrusion. This system was slow but had one advantage in that both sides of the extrusion could be examined for obvious flaws.

We made a small 36-in.-long air-vein fixture for small tubular extrusions. In this case, the graphite fixture had six grooves and the extrusions were not transferred to a separate curing fixture. The metal fixture holder was connected to the air supply and built so that the graphite air-vein fixtures could be readily clamped in place. The loaded fixture was removed from its metal holder, a top was placed on it, and the assembly was placed in the curing oven. Fig. 10 shows a small fixture assembly.

Effects of Pre-Extrusion Conditions

The term "pre-extrusion" is used to describe the extrusion operations that occur before extrusion of the final fuel element. The pre-extrusion process was used as a densifying procedure, and it tended to

UNCLASSIFIED

UNCLASSIFIED

Fig. 10. Small "air-vein" extrusion fixture.

work and homogenize the material before extrusion of the final shape. In most cases, we found that optimum properties such as maximum density and minimum permeability were attained if the mix was pre-extruded three times through a die and the final shape was formed during a fourth extrusion.

To try to minimize the wear on the production tooling we established an extrusion procedure in which the first three extrusions were made through a simple tubular die. The die consisted of a breaker plate containing 1/8-in.-diam holes and a tubular nozzle whose cross section was similar to that of a 19-hole extrusion. The fourth extrusion was made through the 19-hole fuel-element production tooling. As far as the extrusion operation was concerned, this procedure worked very well. However, data obtained later on these same extrusions indicated that the elements had lower densities and leak rates several times those of previous elements extruded four

times through the production tooling. The density of elements made later increased, and the leak rates (permeability) returned to the more normal values obtained before use of the tubular pre-extrusion tooling. Although this effect was not explored in great detail, it is apparent that the amount of working imposed on the extrusion mix is reflected in the properties of the final extrusions. The 19-hole extrusion die does work the material severely, evidently much more than does the circular extrusion die.

Permeability

After the outside surfaces of a graphitized fuel element were machined, we measured the leak rate (permeability) by pressurizing all the holes in the element with 10-psig air. The volume of air required to maintain this pressure was measured. This technique measured only the leak rate between the outer 12 holes and the outside of the element, a relatively thin web. It gave no accurate indication of the condition of the webs between the holes.

We measured the leak rate of over 500 (U,Zr)C-graphite composite fuel elements whose uranium loadings were 102 to 267 mg/cm³. All elements contained 30 vol% total carbide, were made with S97 graphite and low-sulfur ZrC, and had undergone the standard pre-extrusion process of being extruded three times through a 19-hole die. The leak rates did not appear to form a pattern relative to loading, but were scattered between roughly 100 and 200 cm³/min.

The measured leak rate of 59 similar elements that contained 500 mg of U/cm³ was 320 cm³/min. This represents the anticipated higher porosity produced when the higher UO₂ loading converts to the carbide with the loss of some carbon as CO.

We leak checked eighty-three fuel elements with uranium loadings of 124 to 200 mg/cm³. They were then processed in the same manner as the fuel elements mentioned previously. However, we used a ZrC powder with a high (5000 ppm) sulfur content. The leak rate of these fuel elements averaged 482 cm³/min, about 3 times that of similar elements made with low-sulfur ZrC. The effect of a high-sulfur impurity in the extrusion mix had not been recognized before this work.

We have mentioned that pre-extruding a mix through a simple die rather than a 19-hole die produced highly permeable elements. It was unfortunate that this procedure and the high-sulfur ZrC

UNCLASSIFIED

UNCLASSIFIED

were used together. It is difficult to find data that will distinguish between these two variables. However, keeping in mind the $482\text{-cm}^3/\text{min}$ leak rate of the high-sulfur elements mentioned above, one may look at the leak rate of two batches of elements made with high-sulfur ZrC and pre-extruding through a simple die. These batches totaled 14 pieces and were loaded with 166 mg of U/cm^3 . The leak rate averaged $642\text{ cm}^3/\text{min}$. These two batches did contain only 25 vol% of carbide, but this should have tended to lower the leak rate. Thus, it seems that both a high sulfur impurity level in the raw materials and inadequate pre-extrusion of the extrusion mix tend to produce highly permeable fuel elements and, furthermore, the effects are cumulative.

We performed an experiment to determine the effects of extrusion speed and of the number of pre-extrusions on the permeability and density of the graphitized fuel elements. The extruded material was a 30 vol% composite containing 102 mg of U/cm^3 . The results are reported graphically in Figs. 11 through 15 and indicate that there is a correlation between permeability and density, as expected, and that the number of times the material is extruded has a major influence on the density and permeability of the final fuel element.

Fig. 11. Permeability vs extrusion speed of elements made using various numbers of pre-extrusions.

Fig. 12. Permeability vs number of extrusions of elements extruded at various speeds.

Some 30 vol% elements made with high-sulfur ZrC, pre-extruded through a simple die, and containing 630 mg of U/cm^3 had leak rates of about $2500\text{ cm}^3/\text{min}$. Each factor noted contributed to the high leak rate.

It was also unfortunate that the high-sulfur ZrC was used in preparation of development lots made with various high-CTE graphite flours and lots containing metallic "sintering aids" such as iron, nickel, and silicon. In general, these elements had leak rates from a few hundred to over $1000\text{ cm}^3/\text{min}$.

Fig. 13. Permeability vs density of elements made using various numbers of pre-extrusions.

UNCLASSIFIED

Fig. 14. Density vs number of extrusions of elements extruded at various speeds.

We made one lot of 13 elements to see if we could purposely increase the permeability by adding wood flour (0.015 g/cm^3) to the extrusion mix. The elements contained 30 vol% carbide and 166 mg of U/cm^3 . We used standard extrusion procedures, as well as low-sulfur ZrC powder. All elements had leak rates greater than $1000 \text{ cm}^3/\text{min}$, indicating that wood flour, indeed, increased their permeability.

Fig. 15. Density vs extrusion speed of elements made using various numbers of pre-extrusions.

Curing and Baking

Some of the development lots of carbide-graphite composite fuel elements were cured and baked using the same heating cycles used to produce graphite fuel elements. We increased the curing cycle from 63 to 93 h, and lengthened the heat treatment to 60 h in going from 200 to 450°C . We made no other significant changes in the thermal treatment to 400°C . An inert-gas flush through the baking furnace was required to prevent oxidation of the ZrC in the extrusions. The relatively poor vacuum that was satisfactory for baking graphite fuel elements was not adequate to protect the ZrC component in the composite fuel elements. An improved vacuum (difficult to achieve with these particular furnaces) or an adequate sweep of inert gas both inside and outside each fuel element would minimize the oxidation problem. The relatively poor vacuum (1 to 10 torr) combined with the inert-gas sweep produced a satisfactory atmosphere for baking composite elements.

High-Temperature Thermal Treatment

Going from graphite to composite fuel elements involved several changes in the graphitizing or high-temperature thermal treatment. The temperatures for carbide-graphite composite fuel elements were much higher, 2700°C as compared to 2250°C for the bead-loaded graphite fuel element. A two-step heat treatment was required for composites, rather than the single heat treatment for graphite elements. The difference in shrinkage of the composite vs graphite fuel element, the vertical graphitizing furnace, the conversion of oxides to carbides, and the formation of $(\text{U,Zr})\text{C}$ solid solution were all factors that contributed to the requirement for a two-stage composite heat treatment.

In the graphite fuel elements, the shrinkage was divided rather evenly among the various thermal treatments, whereas the composite fuel elements shrank most above 2000°C . The vertical furnace enhanced the distortion because, as the fuel elements shrank, space was created in the vertical fixture into which the fuel element could move, resulting in bent or twisted fuel elements that would not survive the subsequent machining operation. A horizontal furnace would minimize this problem because the fuel element presumably would just drop lower into the fixture as its dimensions decreased. The full-length ($\sim 55\text{-in.}$) fuel element delivered to the shop

for machining must have less than 0.015-in./in. bow and less than 0.006-in. twist over its entire length if it is to go through the hexagonal milling arrangement without breaking and is to meet the final machined specifications.

Conversion of the oxide to the carbide occurs at 1500 to 2000°C with the evolution of considerable quantities of CO gas, the quantity increasing with increased uranium loading. We decrease the heating rate significantly in going through this temperature range, to minimize or eliminate buildup of gas pressure within the fuel elements which could cause cracking or spalling. After the oxide has been converted to carbide, enough time must be allowed at 2350°C for the UC and ZrC to diffuse and form the solid-solution (U,Zr)C. This constitutes the first stage of the two-stage heat treatment. Note that problems related to the oxide-carbide conversion do not exist if solid-solution UC-ZrC particles are incorporated into the extrusion mix. Most fuel-element shrinkage occurs in the first-stage heat treatment, and the element is transferred to another, tight-fitting fixture for the final heat treatment. Here additional time is permitted at 2350°C, on the way up to 2700°C, to make sure that the solid-solution (U,Zr)C has been formed. X-ray diffraction data indicate that, usually, a single-phase solid solution is present after an element has been held at 2350°C for a few hours. At times, two phases of solid solution are present. The temperature is increased to the maximum desired for the particular uranium loading, at which time densification and shrinkage occur, as well as some change in the structure of the carbonaceous materials in the extrusion. If the high firing temperature has been close to or above the solidus temperature, x-ray diffraction almost always reveals two phases of solid solution. The maximum temperature vs uranium loading vs structure is among the important parameters of composite fuel-element fabrication still being studied at LASL.

Hole Sizes and Locations

The abrasive nature of the composite fuel elements, coupled with the small-diameter, 52-in.-long coolant holes, made finishing the 19 holes in the fuel element very difficult if grinding, reaming, or other procedures were required. Consequently, one of the aims of the composite development program was to produce fuel elements with the 19 holes at the

desired diameter after the high-temperature heat treatment. A hole-size tolerance of ± 0.001 in. was specified. The hole-location tolerance specified that all holes were to be within ± 0.006 in. of their true location.

The proper location of the pins in the die can be determined only after the shrinkage of the product is known. Thus, the proper volume percent of loading must be obtained, the raw materials making up the extrusion must be characterized and standardized, and the heat-treating regime must be constant.

There are three families of pins plus the center pin in a 19-hole extrusion die. The theoretical distance from any hole in a family to the center of the element cross section is the same. The percentage of radial shrinkage during heat treatment, i.e. the percentage of change in distance from any hole in a family to the theoretical center of the element cross section varies for each family. This shrinkage affects the final hole location in an element. The families of pins are the six around the center hole, the six corner pins, and the six pins on the flats between the corner pins. The corner holes had the highest percentage of radial shrinkage, the holes around the center hole somewhat less, and the holes on the flats the least.

The individual diametral hole shrinkage, the difference between the die pin size and the final hole size in the heat-treated element, also varies according to pin family, and there is a still different shrinkage of the center hole. The highest shrinkage is in the center hole, with decreasing shrinkage of the six inner holes, the six holes on the flats, and, finally, the corner holes.

The hole sizes in both development and production fuel elements are measured using an air probe. The size determined by the air probe is a fraction of a mil smaller than the same diameter measured using a conventional hole gage.

We determined the shrinkage across the flats of the hexagonal fuel element at each step in the heat treatment. This was necessary in order to provide close-fitting fixtures for the elements at each step. After the final heat treatment, the desired element size was such as to allow 10 to 15 mils of cleanup on each of the hex surfaces to provide the finished element size.

Remember that element shrinkage depends on starting materials, extrusion-die design, extrusion procedure, heat-treating cycles, final heat-treating temperature, and volume percent of carbide and uranium loading. If a wide range of uranium content is required at some specific volume percent of loading, it may be necessary to use more than one set of extrusion tools to accommodate the required pin sizes and hole-location changes.

The hole-size and -location results obtained on the composite fuel elements have been quite encouraging. The hole sizes were measured both by air probe and air flow. The air probe and air flow were used after the elements had been heat treated and machined, whereas only the air flow was used after the bores had been coated with ZrC. The air probe could not be inserted into coated bores because of the possibility of damaging the coat, and, furthermore, the measurements were not meaningful because of variations in diameter along the length of the coated bore.

The air-probe-determined hole sizes of heat-treated, machined elements (the bores were not machined) were practically always within ± 0.001 in. of a nominal diameter. During the process of making hundreds of elements, the nominal diameter did shift slightly, a mil or two, because of die wear and shrinkage factors mentioned previously. In many development lots made later in the program, the hole sizes were within ± 0.0015 in. of a nominal diameter, but they sometimes varied as much as ± 0.002 in. As all bores were coated with ZrC, the coating thickness also affected the final hole diameter. The actual hole diameter was not extremely critical because the propellant flow through each hole in each element was controlled by orifices, sized for each hole diameter, at the inlet end of the element.

The hole locations were measured on a thin (1/16-in.-thick) wafer, usually taken from one end of the element. The wafer was placed in a shadow-graph, and the projected image was compared to a template with marks indicating the desired hole locations. A large majority of holes were within 4 mils of their desired location. Practically all were within 6 mils (the class I element tolerance). Meeting hole size and location tolerances has not been a major problem in the manufacture of carbide-graphite composite fuel elements.

Brazing

During the development of the composite fuel element, situations arose that called for brazing tips onto fuel elements or brazing together different types of elements. Consequently, we undertook some development work to cover brazing problems for these two cases. We brazed fuel elements to tips, to other fuel elements having different volume percent loadings, and to bead-loaded elements. The tips were machined from hot-pressed NbC-TaC-C composite material containing 46 vol% carbide. When brazing fuel elements to tips, we placed a transition piece of 30 vol% ZrC-C composite material between the tip and the element. We brazed the tip to the transition piece and brazed this assembly to the fuel element, in two separate operations. The transition piece of 30 vol% ZrC is necessary because of the Mo-UC₂ low-temperature eutectic that would produce a liquid component at the 2650°C brazing temperature desired for molybdenum. Therefore, the refractory carbide composite tip material is brazed to the 30 vol% ZrC transition piece using molybdenum at 2650°C, after which this assembly is brazed to the fuel element at 2350°C using (U,Zr)O₂ powder.

A very brief summary of brazing conditions is given in Table II. The 0.7-mil molybdenum brazing medium was molybdenum powder on a plastic tape. The powder side of the tape was placed on one of the surfaces to be brazed, the plastic surface was rubbed to transfer the powder to the brazing surface, and the tape was removed. The two surfaces to be joined were then clamped together and heated inductively.

The (U,Zr)O₂ joining medium was -325-mesh powder produced by oxidizing (U,Zr)C solid-solution powder. This powder contained 10 mole % of UC (D-38). The surfaces to be brazed were wet with Varcum, the excess Varcum was wiped off, and the surfaces were dipped in the (U,Zr)O₂ powder. The pieces were tapped to remove any excess (U,Zr)O₂ powder, and the surfaces were clamped together and heated. Braze joints generally were quite strong, having moduli of rupture in flexure between 3000 and 8000 psi.

Graphite-brazing development is reported in LA-3960.³ Composite-brazing development has been reported in IASL Rover Quarterly Reports from Nov. 30, 1968 to May 31, 1970.

UNCLASSIFIED

TABLE II

BRAZING CONDITIONS FOR COMPOSITE FUEL ELEMENTS

Materials Joined	Joining Medium	Brazing Temp (°C)	Time at Temp (min)
30 vol% ZrC-C to 30 vol% ZrC-C or 46 vol% (Ta,Nb)C-C tips	0.7-mil Mo	2650	1
30 vol% ZrC-C to 30 vol% (U,Zr)C-C	(U,Zr)O ₂	2550	5
36 vol% ZrC-C to 36 vol% ZrC-C or 36 vol% (Zr,Ta)C-C	0.7-mil Mo	2650	1
30 vol% (U,Zr)C-C to LASL or WANL high-CTE bead-loaded elements	(U,Zr)O ₂	2350	10
30 vol% (U,Zr)C-C to 50 vol% (U,Zr)C-C	(U,Zr)O ₂	2550	10
40 vol% (U,Zr)C-C to 50 vol% (U,Zr)C-C	(U,Zr)O ₂	2550	10
40 vol% (U,Zr)C-C to WANL high-CTE bead-loaded elements	(U,Zr)O ₂	2300	10

Central Support Elements

One-hole hexagonal center-support elements were extruded and heat treated like composite fuel elements. The 36 vol% ZrC loading was added to the extrusion mix as ZrC powder. Some elements contained 230 mg of tantalum/cm³ as a neutronic poison, but the total carbide loading of 36 vol% was maintained. The carbides were added to the mix as ZrC and TaC powders. There is no uranium in these support elements.

The elements were extruded with a minimum wall thickness of 0.083 in. between the center hole and the flat of the hexagon. Other than being rather weak and tending to be a little out of round, these elements developed little trouble during extruding and processing. Tip stock for the elements had a minimum wall thickness of 0.200 in. During heat treatment, these extrusions tended to blister, spall, and laminate because of the thicker section and the difficulty in removing gasses. Only by adding wood flour to the extrusion mix could we make satisfactory pieces.

SUMMARY

Nineteen-hole carbide-graphite composite fuel elements containing various amounts of (U,Zr)C (usually 30 vol%) were made successfully. We could extrude the 19 holes to a given size so that they did not have to be reamed. Mix calculations, extrusion mixes, extrusion procedures, and heat-treating cycles were developed to produce relatively flaw-free elements having the desired uranium loading and carbide content.

Techniques were developed for brazing the composite elements to composite tips and to other elements. A die-wear experiment resulted in the selection of Ferro-Tic as a wear-resistant extrusion-die material.

ACKNOWLEDGMENTS

Engineering support in the design of dies, fixtures, and furnaces for this program was provided by Group CMB-7 and especially by S. J. Bustamante, D. E. Hull, and M. T. Esquibel.

Further support was provided by Groups CMB-1 in chemical analyses, CMB-3 in heat treating, coating, and x-ray diffraction, GMX-1 in nondestructive testing, N-1 in element evaluation, and the Shops Department in machining and inspection.

REFERENCES

1. W. W. Martin, D. H. Schell, J. M. Taub, and J. W. Taylor, "The Fabrication of Uranium-Loaded Graphite Fuel Elements for Kiwi-B4/B5 Reactors," Los Alamos Scientific Laboratory report LA-2936 (1963). Conf. RD.
2. R. E. Riley, N. K. Richerson, and D. H. Schell, "Extruded Carbide-Graphite Composites," Los Alamos Scientific Laboratory report LA-4077 (1969).
3. D. J. Sandstrom, "Joining Graphite to Graphite with Transition Metal Foils," LASL report LA-3960 (1968).

We had to establish a uniform method of calculating the amounts of the various ingredients required to make up an extrusion mix. The usual method of expressing the desired content of an extrusion was to specify the volume percent of (U,Zr)C and the milligrams of uranium per cubic centimeter required in the final product. We made two arbitrary assumptions to ease the calculations. We assumed that the (U,Zr)C was stoichiometric and was present in the extrusion at theoretical density. We also assumed that the density of the (U,Zr)C solid solution did not change from that of the individual carbides. These assumptions placed all of the extrusion's porosity in the free-carbon part of the composite. There were rather large variations in the free-carbon density as the volume percent of loading changed. Free-carbon density was expressed in grams per cubic centimeter in the volume it occupied, in other words, in the volume not occupied by the (U,Zr)C.

One can readily see that the uranium loading and volume percent of loading depend not only upon the mix calculations but also upon the shrinkage of the elements during thermal treatment. It was desirable that the elements have uniform dimensions along their length so that a sample would represent the complete element. This was not always true because of extrusion problems (taper) and heat-treatment temperature gradients, as mentioned previously. Therefore, until the variables settled down so that the scatter in the analytical data diminished, we could not make an accurate extrusion-mix calculation. Even today, because of unknown variables and the use of new (high-CTE) graphite flours that have different shrinkages, the uranium loadings may be off by a few percent.

We based all calculations on 1 cm^3 of the final heat-treated, machined product. The loadings, both uranium and carbide, for all development work were determined by chemical analyses, whereas the uranium content of production elements was determined both by chemistry and incremental gamma counting. Because the calculations were based on 1 cm^3 of product and because the desired uranium content was expressed in milligrams per cubic centimeter, it was a simple matter to calculate the amount of UO_2 required for 1 cm^3 of product. The

be formed was calculated and subtracted from the volume of (U,Zr)C specified. The remainder was the volume of ZrC at theoretical density required, which readily gave the weight of ZrC required.

We had to predict the free-carbon density in the final product, as mentioned previously. This varied in relation to the volume percent loading of (U,Zr)C and also to uranium loading at a constant volume percent. The carbon density decreased as the uranium loading increased, partly because of the loss of carbon and the porosity formed when the UO_2 converted to the carbide. Free-carbon densities, as determined by immersion densities and chemical analyses of extrusions, were plotted vs uranium loading at similar volume percents. The volume percents were seldom exactly as predicted but were usually within a few percent of that desired. For example, for a nominal 30 vol% curve, free-carbon densities were plotted against uranium loadings for extrusions containing 28 to 32 vol% of carbide. We used these curves in predicting carbon densities in subsequent extrusions. Such a curve is shown in Fig. A-1.

Knowing the free-carbon content in an extrusion and calculating the carbon required to convert the UO_2 to UC, one knows the total carbon requirement for an extrusion mix. This carbon comes both from the carbon addition to the extrusion mix (graphite flour plus Thermax) and the carbon residue left by the Varcum binder. It then becomes necessary to have a uniform method of calculating the required binder for the mix. An obvious criterion for the binder content is the amount required to form an extrudable mix. It is also obvious that a specific amount of binder is required for extrudability, regardless of the method used to calculate this requirement.

We considered different methods for calculating binder requirements. They could be calculated on a weight or volume basis, or by using some property of the dry ingredients in the mix. The binder requirement for graphite extrusions is based on the dry ingredient weight. For bead-loaded graphite extrusions, we use a more complicated formula, but basically the binder requirement is still determined by weight. Experience in making extrusions has developed a certain feel for adjusting the binder to obtain the proper mix consistency. If this

UNCLASSIFIED

UNCLASSIFIED

Fig. A-1. Free-carbon density vs uranium loading for a 30 vol% composite.

experience could be carried over to the composite extrusions, it would be very useful. Also, the data required to make the binder calculations must be readily available; especially for development extrusions.

Basing the binder content on the dry-ingredient weight of a composite mix would mean that the percentage of binder usually would be very low compared to that for a graphite extrusion and would vary considerably as the volume percent of loading varied. This is because of the relatively high density of the UO_2 and ZrC compared to graphite. Also, at some specific volume percent of loading, the percentage of binder would vary as the uranium loading varied. This may be true regardless of the method used to calculate the binder requirement, but we felt that this variation should be minimized.

We decided to base the binder content in the composite mix calculations on the "bulk" volume of the dry ingredients in the mix. We therefore had to obtain "bulk" densities for these ingredients. We assumed the density of the carbon addition to be

1.0 g/cm^3 . We obtained the density of the other ingredients from the porosity number obtained when the average particle size of the powder was measured on a Fisher Sub-Sieve Sizer. The powder sample, 1 cm^3 at theoretical density, is lightly compacted for the Fisher measurement, and the porosity of the compact is read off of a scale. This number is subtracted from 1, and the difference is multiplied by the theoretical density of the material to give a "bulk" powder density. Actually, this density is closer to a "tapped" powder density. Because the average particle size of all powders is measured before their use, the Fisher porosity is always available. The amount of carbide and oxide required in the extrusion divided by the appropriate bulk density gives the bulk volume of these powders. This volume multiplied by the binder number gives the amount of binder required for extrusion of these ingredients, the carbide and oxide only.

The next somewhat elusive number required is the coking value, or percent of carbon residue left in the extrusion by the Varcum binder. A true coking value measured on the binder itself probably is not correct. The residue left by the binder in an extrusion probably will vary with the particular mix and type of extrusion. The residue in unloaded extrusions probably will differ from that in composite extrusions, and 1-hole and 19-hole elements may differ. The carbon residue figure used for all extrusions to date is 45 wt% of the Varcum binder. This was based on chemical analyses of unfueled composite extrusions for which an overall weight balance was obtained.

The weight of binder required for the carbide and oxide is known (above), and the binder residue value is known, so the carbon residue from this amount of binder is known. This is subtracted from the total carbon requirement mentioned previously, leaving the amount of carbon to be added to the mix as free carbon and the carbon residue from the binder required for extrusion of the free carbon. Using the same binder number as for the carbide and oxide and the same carbon residue number for the binder, one can calculate the amount of free carbon and binder remembering the assumption that the "bulk" density of the free carbon is 1.0 g/cm^3 . This completes the calculation of the ingredients to be

mixed to produce 1 cm³ of fuel element. The calculation for composite hardware shapes is similar except that the UO₂ and the carbon required to convert the UO₂ to UC are eliminated.

The binder number, usually around 0.33, is really the grams of binder required for extrusion of 1 cm³ of dry ingredient. Experience showed that this number changed very little, from 0.32 to 0.35, for a 20% change in volume percent of loading and uranium loadings of 102 to 630 mg/cm³.

The final step in the batch calculations was to multiply the amounts of the various ingredients required in 1 cm³ of product by the batch size; usually 2000 to 3000 cm³. This was a convenient volume to blend in the 16-qt twin-shell blenders.

Chemical analysis of several batches of 30 vol% 19-hole elements having a loading range of ~100 to 600 mg of uranium/cm³ showed that there was a bias between the calculated and actual loadings. The actual loadings were higher than they should have been according to the batch calculations. This bias for loadings of 100 to 400 mg/cm³ amounted to about 6% and decreased slightly for loadings up to ~600 mg/cm³.

The actual loadings were plotted against the calculated loadings, and this curve, Fig. A-2, was used to determine the correction for future calculations. The reason for the bias is not known, but it could be a cumulative effect of minor variables that are not taken into account in the batch calculations. For instance, we assume that the UO₂ and ZrC powders are stoichiometric, but they really aren't. Chemical analyses of the total and free-carbon contents of heat-treated extrusions show that the (U,Zr)C is always slightly substoichiometric. Also, the coking value of Varcum probably is not always exactly 45%. We felt that it was simpler to make a small correction in the uranium loading of the batch calculation than to complicate the calculations with a number of trivial adjustments.

Batch calculations for production extrusions have been set up on a computer program, MATY. The calculations to obtain the uranium loading, the volume percent of carbide, and the free-carbon density from the chemical analyses have also been programmed, in MASH.

Fig. A-2. Uranium-loading correction curve for 30 vol% composite.

A sample hand calculation for a 30 vol% composite mix is shown in Table AI. The various factors and constants used in the calculations are as follows.

Desired uranium loading, 0.251 g/cm³

Loading used in the batch calculations, 0.237 g/cm³, from the loading correction curve, Fig. A-2.

Factors	Purposes
1.136	Converts U wt to UO ₂ wt.
0.153	C needed to convert U as UO ₂ to UC.
1.051	Converts U wt to UC wt.
13.6	Density of UC, g/cm ³ .
6.6	Density of ZrC, g/cm ³ .
3.584	Bulk density of ZrC, g/cm ³ .
6.028	Bulk density of UO ₂ , g/cm ³ .
1.642	Density of the free C in the final product, g/cm ³ , from Fig. A-1.
0.45	Varcum wt to residual C wt.
0.35	Binder number, g of binder/cm ³ of dry ingredient bulk volume.
0.864	This amount of free C plus the C from the binder required to extrude this free C will produce 1.0 g of total C when the above binder number and Varcum residual factor are used.
1.0	Bulk density of C, g/cm ³ .
2670	Batch size, cm ³ of product.

APPROVED FOR PUBLIC RELEASE

TABLE A1. SAMPLE MIX CALCULATIONS FOR 50 VOL% COMPOSITE

$0.237 \text{ g} \times 1.136$	=	0.269 g UO_2
$0.237 \text{ g} \times 0.153$	=	$0.036 \text{ g C needed, UO}_2 \rightarrow \text{UC}$
$0.237 \text{ g} \times 1.051$	=	0.249 g UC
$0.249 \text{ g} \div 13.6$	=	$0.018 \text{ cm}^3 \text{ UC}$
$0.30 \text{ cm}^3 - 0.018 \text{ cm}^3$	=	$0.282 \text{ cm}^3 \text{ ZrC}$
$0.282 \text{ cm}^3 \times 6.6 \text{ g/cm}^3$	=	1.861 g ZrC
$1.861 \text{ g} \div 3.584 \text{ g/cm}^3$	=	$0.519 \text{ cm}^3 \text{ ZrC (bulk)}$
$0.269 \text{ g} \div 6.028 \text{ g/cm}^3$	=	$0.045 \text{ cm}^3 \text{ UO}_2 \text{ (bulk)}$
		<hr/>
		0.564 cm^3 , bulk volume of ZrC and UO_2
$0.70 \text{ cm}^3 \times 1.642 \text{ g/cm}^3$	=	$1.149 \text{ g free C in product}$
$0.564 \text{ cm}^3 \times 0.45 \times 0.35 \text{ g/cm}^3$	=	$0.089 \text{ g Varcum C residue from Varcum needed to extrude UO}_2 \text{ and ZrC}$
		1.060 g C
		<u>0.036 g C</u>
		$1.096 \text{ g C} \times 0.864 = 0.947 \text{ g free C in the mix}$
$0.947 \text{ g} \div 1.0 \text{ g/cm}^3$	=	$0.947 \text{ cm}^3 \text{ free C (bulk)}$
		$0.564 \text{ cm}^3 \text{ (bulk) of ZrC and UO}_2$
		<hr/>
		$1.511 \text{ cm}^3 \times 0.35 \text{ g/cm}^3 = 0.529 \text{ g Varcum}$
Weight (g) of mix ingredients for 1 cm^3 of product		Weight (g) of ingredients for one 2670-cm^3 blender load
0.947	S97 Mix	2528.
1.861	ZrC	4969.
0.269	UO_2	718.
0.529	Varcum	1412.

UNCLASSIFIED

RECEIVED

OCT 26 '72

LASL LIBRARIES

UNCLASSIFIED