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ARMY GAS-COOLED REACTOR SYSTEMS PROGRAM

**SUMMARY REPORT ON MATERIALS
FOR THE GCRE-II**

30 DECEMBER 1960

Aerojet-General NUCLEONICS

A SUBSIDIARY OF AEROJET-GENERAL CORPORATION

SAN RAMON, CALIFORNIA

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ARMY GAS-COOLED REACTOR SYSTEMS PROGRAM

SUMMARY REPORT ON MATERIALS
FOR THE GCRE-II

by
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and
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SUMMARY REPORT ON MATERIALS FOR THE GCRE-II

ERRATA

- P. 11, Pgh 3 Last sentence should read: "However, no data on the diffusion rates of UC into the carbides are available to support this."
- P. 13, Fig. 4 Ordinate: "Uranium Concentration, mg/cc".
- P. 18, Pgh 7 Second sentence should read: "The final firing temperature is much below that at which UO_2 coated with either AlO_3 or BeO will begin to react with carbon."
- P. 19, Sec. 3 Equation should read: $k = \frac{q \ln (a_2/a_1)}{2 \pi L (\Delta T)}$
- P. 21, Fig. 5 Ordinate, left: "Temperature, $^{\circ}\text{F}$ "; right: "Temperature, $^{\circ}\text{C}$ ".
- P. 23, Fig. 6 Ordinate: "Tensile Stress, psi".
- P. 40, Pgh 4 In the tabulation of properties of reagents, line 1 should read: "HF attacks SiO , SiO_2 ; will not attack Si_2C , SiC , Si ." Line 2 should read: " HNO_3 attacks Si_2C ; will not attack Si , SiO , SiO_2 , SiC ."
- P. 47, Pgh 3 Second sentence should read: "It is tentatively identified as a 5 mil layer of silicon, a 1 mil layer of SiC containing Si_2C inclusions and a 40 mil layer of SiC particles or islands (containing Si and Si_2C inclusions) dispersed in a graphite matrix proceeding inward from the air-silicon interface."
- P. 49, Pgh 1 Last sentence should read: "Although the interlayer must also maintain a fair amount of ductility and strength, data on compatibility with graphite and effects from thermal cycling at a temperature of 1850°F became a primary requirement."
- P. 49, Pgh 5 In line 5, "vacuum of 10 microns" should be changed to read: "a partial vacuum".
- P. 52, Line 6 & P. 61, Pgh 6 Change "0.1/min" to read: "0.1 in./min".
- P. 64, Table 8 Sample 3 was discarded. The line "Same as above" under heading "Remarks on Exposed Samples" should be deleted.
- P. 67, Pgh 3 Change to read: "Mixes used in joint fabrication were applied on bare graphite surfaces and on surfaces impregnated with Mixture 3."

ABSTRACT

This report summarizes investigations of various materials for development of metal canned and semi-homogeneous GCRE-II fuel element concepts. The materials were studied for application to development of fuels, graphite, silicon-silicon carbide coatings, metal claddings, carburization barrier coatings, and graphite joining.

A survey of the literature has shown that uranium carbide fuels are superior to other types for the applications described and that refractory metal or metal carbide fuel coatings appear superior to other types for use with the types of graphite investigated.

Experimental measurements were made of the thermal conductivity, tensile strength, stress-strain relationships, and thermal expansion of graphite powder bonded with baked carbon at a final firing temperature of 760°C. Results showed that these materials were stronger and more isotropic at all test temperatures than a standard structural graphite such as ATJ. The thermal conductivity is somewhat lower and the thermal expansion slightly higher than the corresponding properties of ATJ.

A silicon-silicon carbide coating was developed as an oxidation resistant coating for graphite. Preliminary air oxidation tests at 1000°C have shown that the first samples survived 2000 hr with 10% failure. Subsequent experiments show that it is reasonable to expect better performance in further tests.

Tests for compatibility with graphite were conducted on zirconium, Zircaloy-2, "A" nickel and K-Monel at 1750 and 1850°F for 1000 and 1500 hr. Chemical analyses, metallography and tensile tests indicate that the K-Monel is the material most compatible with graphite; it possesses good strength and ductility with negligible carburization or carbon diffusion.

Zircaloy-2 tubing showed a growth of from 3.4 to 3.8% when thermal cycled 100 times between 850 and 1850°F.

Tests for compatibility with Hastelloy X were conducted on graphite samples coated with molybdenum, niobium carbide, and zirconium carbide at 1750°F and 300 psi for 1000 and 1500 hr. Chemistry and metallography indicate that all coatings tested would function

satisfactorily as carburization barriers to Hastelloy-X.

Graphite joints using various fillers and binders were fabricated and tensile-tested at room temperature. Joints using a selected combination of C-6 filler and polymerized furfuryl alcohol as binder produced maximum tensile strength of 2000 psi.

I. INTRODUCTION

GCRE-II is a portable gas-cooled low power reactor with fuel elements composed wholly or partially of a homogeneous dispersion of uranium in graphite. The end-product fuel for this reactor must permit little or no fission product release to the coolant gas during operating lifetime. The most advanced form of the fuel will be capable of operation in air; the immediate objective is operation in an artificial atmosphere of 99.5 vol % N_2 + 0.5 vol % O_2 .

The fuel materials utilized must be fabricable, possess adequate strength and be compatible at design conditions. The thermal conductivity of the assembled element must be high enough to prevent an excessive radial temperature drop within the fuel element.

This report covers material studies conducted up to 1 August 1960 in support of the GCRE II program, and describes investigation of fuels, graphite, silicon-silicon carbide coatings, metal cladding, carburization coatings and graphite joining.

The selection criteria for materials for all of the applications listed above are not independent variables. Because fission product retention is important to the GCRE-II concept, the temperature at which the fuel is processed has been selected as the basic independent variable for selection of both fuel and graphite.

Therefore, non-standard low temperature graphites were investigated and the literature was relied on for properties of normal fully graphitized graphite.

The success of the silicon-silicon carbide coating is somewhat dependent upon close agreement between the thermal expansion coefficient of the base graphite and that of the coating.

Carburization barrier coatings do not have a great effect on the fuel-graphite choices, although the application temperature for such coatings must be lower than fuel-processing cycle temperature.

The major problem with metal cladding is compatibility with carbon or with an interposed carburization barrier coating.

Graphite joining is limited only by permissible process temperature.

Advanced concepts have shown that, by selection of various graphite matrix fuel element designs, higher efficiency and power density than those of the present ML-1 could be achieved with higher operational temperatures.

The most promising system studied used a semi-homogeneous graphite matrix fuel element. This type of fuel element consists of a fueled graphite cylinder encased in a metal can. This can is placed in an unfueled external graphite cylinder which provides the necessary structural support to withstand the dead load of the fuel element array. The metal can provides an impermeable barrier to fission products and does not have to possess a great deal of structural strength. A silicon-silicon-carbide coating on the outside surface of the unfueled graphite cylinder prevents corrosion and erosion by the coolant gas. A cross section of the semi-homogeneous fuel element is shown in Figure 1.

In an earlier concept, a metal can was designed to provide retention of fission products and structural support. For this application, a metal such as Hastelloy-X, possessing strength and oxidation resistance at lower operational temperatures, appeared promising. However, it was considered possible that carburization could occur if the metal can and graphite were not compatible. This necessitated further investigation to determine whether a barrier coating on the graphite would be required to prevent carburization.

The design parameters for the metal canned and semi-homogeneous fuel element concepts are as follows:

<u>Parameters</u>	<u>Metal Canned</u>	<u>Semi-Homogeneous</u>
Temperature (max) of Metal	1750°F	2100°F
Temperature (max) of Fuel	1950°F	2400°F
Core Size	24 in. dia x 24 in. long	31 in. dia x 33 in. long
Fuel Loading (U-235)	32 kg	25 kg
Pressure	400 psia	400 psia
Temperature Reactor Outlet	1400°F	1300°F
Coolant Gas	Nitrogen + $\frac{1}{2}\%$ O ₂	Nitrogen + $\frac{1}{2}\%$ O ₂
Flow Rate	90,000 lb/hr	470,000 lb/hr
Void Fraction	15%	15%
Metal Fraction	9%	3%
Power (thermal)	4.0 Mw	16 Mw
Reflector	BeO	BeO

SEMI-HOMOGENEOUS FUEL ELEMENT

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II. FUEL DEVELOPMENT

A. FUEL

The GCRE-II fuel element, whether homogeneous or semi-homogeneous, will be fueled with a homogeneous dispersion of UC or UO_2 particles 100 to 150 microns in diameter, coated with 10 to 20 microns of a refractory oxide, metal or carbide, compatible with both fuel and graphite at operating and process temperatures.

The fuel must contain approximately 10 wt % fully enriched UO_2 or UC, be capable of 12 atom % burnup at 2000°F and must not have a fission product release ratio* greater than 10⁻¹⁰.

Harrison, et al (1)** have investigated the fraction of recoils and fission fragments that will escape from a spherical particle of fissionable material as a function of particle radius. The results of his calculations (Figure 2) show that, for a particle radius of 100 microns, approximately 14% of the fission products will be released from the fuel particle immediately or soon after fission.

From these results, Harrison predicted that fission damage to the matrix, using UO_2 particles of 100 micron diameter, would be about 5% of the damage which would result from the homogeneous case. (2) The principles on which these calculations are based are general; by substituting the appropriate numbers, a similar curve can be derived for any uranium compound.

* Fission product release ratio is defined as R/b where R = the concentration of a selected fission product or products in the sweep gas of an in-pile loop, and b is the calculated number of such isotopes "born" during the in-pile test at a specified time and temperature.

** (1) Arabic numerals in parens refer to the references listed at the end of this report.

On the basis of this work it was decided that the fuel particles used in the GCRE-II graphite matrix dispersion should be no smaller than 100 microns diameter. This section of this report discusses reaction characteristics of two fuels with graphite and the stability of several materials that could be used for coating the fuel to prevent such reactions and/or fuel diffusion throughout the graphite matrix.

B. REACTION CHARACTERISTICS OF URANIUM COMPOUNDS WITH GRAPHITE

1. Reaction Between Graphite and UO_2

Carbon will completely reduce UO_2 to the monocarbide at 1800°C , with the evolution of CO. The reaction is very slow below about 1200°C ; the rates are influenced by the particle size of the oxide. If hyperstoichiometric oxide is used, the removal of excess oxygen will proceed at temperatures below 1000°C .⁽³⁾

The data presented in Table 1 were obtained by mixing -60 to +80 mesh UO_2 in lampblack and heating in a system purged continuously in argon.⁽⁴⁾

TABLE 1

RESULTS OF UO_2 -GRAPHITE COMPOSITE REACTION TESTS

<u>SAMPLE NO.</u>	<u>TEMP $^\circ\text{C}$</u>	<u>TIME HELD AT TEMP (HR)</u>	<u>WEIGHT LOSS (%)</u>	<u>WEIGHT LOSS DUE TO OXIDATIONS (%)</u>	<u>COMPOUNDS PRESENT</u>
102	2200	0	11.86	0.66	UC, UC_2
182	1835	0	10.24	0.65	UO_2 , UC, UC_2
258	1425	19	1.56	1.00	UO_2 , UC
252	1425	89	5.31	1.10	UO_2 , UC
253	1425	89	2.88	1.10	UO_2 , UC
263	1350	72	1.08	1.51	UO_2

If conversion of the UO_2 to UC were complete and no carbon were lost by oxidation from gaseous impurities, the weight loss would be 10.38%.

a. The Carbon-Uranium System

Uranium and carbon form three carbides: UC, with 4.8% C; U_2C_3 , with 7.0% C; and UC_2 , with 9.3% C. U_2C_3 is unstable, decomposing to the other two carbides at above 1800°C . UC melts at 2350°C - 2400°C and UC_2 at 2450°C - 2500°C .^(5,6)

The uranium carbides are produced by reacting a powder mix of uranium dioxide and carbon at above 1800°C . Any form of uranium dispersed in carbon and heated above 2200°C will form UC_2 . UC_2 is unacceptable for the applications discussed here since it is more reactive than UC and has a lower uranium density. If the rate of temperature decrease is controlled by holding the temperature for several hours at 1800°C , then all of the UC_2 should be transformed to UC.

2. Reaction Between Graphite and UC

Several laboratories have found that migration of uranium, in the form of carbides, is severe during fabrication at graphitization temperatures.⁽⁷⁾ In investigations of migration, carbon elements 1/2 in. in diameter by 3/4 in. long containing 0, 5, 25 and 50 wt % UO_2 , and previously baked at 700°C , were placed on a graphite slab within a capsule. The capsule was flushed with argon at the rate of 3 liters/min while the samples were being heated to 2800°C . The final temperature was reached in approximately 2 hr. Inspection of the sample loaded with 50 wt % UO_2 showed globules of UC on the outside of the capsule. All lots of uranium-loaded graphite elements heated to 2600°C showed bulk losses of from 5% to 10% of uranium after 10 min. There is an indication that the uranium loss is controlled by the amount of surface area available for⁽²⁾ evaporation and not by the method of incorporation in the graphite.

It is also indicated⁽²⁾ that uranium promotes graphitization of resin cokes and that it is more effective in the form of fine particles when it can permeate the graphite freely.

Solid phase diffusion of uranium through graphite is negligible at temperatures lower than 1450°C .^(8,9)

The diffusion experiments of Loch, Gambino and Duckworth⁽¹⁰⁾ show that at temperatures less than approximately 2350°C , volume diffusion of uranium through graphite is not a serious problem at distances greater than 0.05 cm from a UC_2 - graphite interface.

There is another uranium transport mechanism observable; this appears to be interconnected pore migration. Such migration is very rapid at temperatures above 2350°C . Within times and temperatures studied, depths of penetration by pore migration are about 10^2 greater than penetrations due to volume diffusion.

There is a steep concentration gradient in the 0 to 0.05 cm region; however, this gradient is localized. For example, a test run at 2100°C for 16 hr showed that the uranium concentration at 0.004 cm from the interface was 1200 mg/cc; at 0.011 cm from the interface the concentration was only 110 mg/cc. Uranium concentrations in the graphite due to pore migration are much less for comparable times, on the order of 100 mg/cc. But such concentrations extend for several centimeters from the interface. It is believed that such long distance

transport of uranium will cause more recoil damage to the graphite than a steep, highly localized concentration gradient. Figure 3 shows the change in uranium transport mechanism. Pore migration becomes the most important transport mechanism at that point of the curve where the slope becomes less negative.

Figure 4, which is plotted to emphasize the change in shape, demonstrates that two mechanisms for fuel diffusion exist, and that such diffusion presents a serious problem during element fabrication at graphitization temperatures. To eliminate the problem, a barrier compound must be found which is inert to both uranium carbide and graphite. The most obvious compounds to investigate are the refractory carbides and possibly a few oxides.

C. REACTION OF UC AND OTHER CARBIDES

Uranium monocarbide forms a continuous series of solid solutions with ZrC and TaC and probably with NbC^(3,11,12,13). Up to 40 mol % of VC and Be₂C will dissolve in UC^(12,6). UC will dissolve between 5 and 10% TiC and WC and less than 5% Cr₃C₂ and MoC⁽¹¹⁾. UC is soluble in ZrC, TaC and NbC, but only slightly soluble in the other carbides mentioned above. Uranium dicarbide is completely soluble with ThC₂⁽⁶⁾. It is probable that the choice of a barrier material will be limited to carbides which are not soluble in UC or in which UC is not soluble; otherwise the uranium will be transferred through the material into the graphite. However, data on the diffusion rates of UC into the carbides are available to support this conclusion.

D. REACTION OF UC WITH METALS

One method of providing a barrier between UC and graphite may be to coat the UC with a metal, and to convert the metal to carbide as the graphite fuel element is heated to the graphitization temperature. This method should be feasible if the reaction between graphite and the metal is much more rapid than that between the UC and the metal.

It has been demonstrated that tantalum and molybdenum are inert with UC up to at least 1760°C^(8,14). Niobium is compatible with UC to at least 1400°C^(*). Titanium begins to react with UC at 1100°C⁽¹⁵⁾. Both Zr and Si react with UC at 1000°C^(8,16). Tungsten is reported to be inert to UC at high temperatures.

Below is a list of reaction temperatures for metal + carbon --> metal carbide⁽¹⁷⁾.

<u>Element</u>	<u>Reaction Temperature</u>
Mo	1200 - 1400°C
Ta	1300 - 1500°C
Nb	1300 - 1500°C
W	1400 - 1600°C
Gr	1400 - 1800°C
Ti	1700 - 2100°C
Zr	1800 - 2200°C

* Private communication, M. G. Bowman, Los Alamos Scientific Laboratory.

TYPICAL URANIUM PENETRATION CURVES IN AGOT GRAPHITE DIFFUSION COUPLE, GRAPHITE: UC_2

DIFFUSION COUPLE: $C_{\text{graph. UC}_2}$
(FROM LOCH, GAMBRINO AND DUCKWORTH)

In case the carbonizing method fails, there is a second approach. Most of the metals listed will form carbides at a lower temperature if a mixture of H_2 and CH_4 or CO is passed over the hot metal. Metal coated UC could be treated by this process, then dispersed in carbon and graphitized.

The properties of the metals and carbides being studied are seen in Table 2.

E. REACTION OF METAL OXIDES WITH UC AND GRAPHITE

Metal oxides also might be used as a barrier material. No experimental data can be found on the reaction between UC and the oxides but thermodynamic data indicate that UC should be compatible with MgO , ThO_2 , and BeO .

The only oxides which are stable when in contact with graphite at high temperatures are ThO_2 and BeO . ThO_2 reacts with graphite at about $2000^\circ C$ and BeO melts below graphitization temperatures. No oxide appears to be compatible with carbon at graphitizing temperatures ($2500^\circ C$).

F. CONCLUSIONS

Literature study and calculations by the authors of this report indicate that, because of the high temperatures involved, the full graphitization process ($>2500^\circ C$) is not suitable for the incorporation of any pure uranium compound such as UO_2 or UC in graphite, if fission product retention is desired.

Further study should be made of diffusion and chemical reaction between graphite and possible fuel coating materials and between UC and possible fuel coating materials.

The literature indicates that the best materials for coating UC for dispersion in fully graphitized graphite are MoC , VC , NbC and ZrC . For a low temperature ($110-1200^\circ C$) baked graphite composite material, such as grade H or O-15, refractory metal coatings on the fuel particles should be compatible, although this has not been verified experimentally. It is believed that molybdenum, titanium, vanadium, niobium and zirconium will offer good fission product retention and that a metal will offer better retention than a metal carbide. However, this requires experimental verification.

Further investigations must be made before a firm decision can be reached on the type of graphite material to be used for fuel dispersion.

TABLE -2- PROPERTIES OF METALS AND CARBIDES

Metals	M.P.(°C)	σ (barns)	Average Coef. of Thermal Exp. ($\alpha \times 10^6 / ^\circ\text{C}$)
W	3410	18.0	5.0 (1000-2500°C)
Ta	3000	22.0	7.2 (500-2500°C)
Mo	2622	2.5	6.2 (500-2500°C)
Nb	2480	1.0	8.8 (500-2500°C)
Cr	1890	3.1	6.2 (20°C)
Zr	1830	0.18	5.0 (20°C)
V	1735	4.9	8.3 (20°C)
Ti	1725	6.0	8.5 (20°C)
Be	1350	0.01	12.4 (20 - 200°C)

Metal Carbides	M.P.(°C)	Average Coef. of Thermal Exp. ($\alpha \times 10^6 / ^\circ\text{C}$)	Solubility in UC
UC	2350-2400	9.5	
UC ₂	2450-2500	13.0	
TaC	3877	8.2	Completely
ZrC	3530	6.7	Completely
NbC	3500	6.8	Almost Completely
TiC	3140	7.4	Up to 10 mol %
WC	2967	6.2	Between 10-20 mol %
VC	2830		Up to 40 mol %
MoC	2692		Up to 5 mol %
SiC	2200	4.3(25-800°C)	
Be ₂ C	2150	10.5(25-600°C)	Up to 40 mol %
Cr ₃ C ₂	1890		Up to 5 mol %

Material	Molar Volume ($\frac{\text{cc}}{\text{mol}}$)	Structure
Mo	9.4	BCC
Ti	10.7	HCP to 885°C, BCC above 885°C
V	8.4	BCC
Nb	10.7	BCC
Zr	14.0	HCP BCC @ $\pm 3^\circ\text{C}$
Mo ₂ C	22.9	Hexagonal complex
MoC	12.7	Hexagonal
TiC	14.1	FCC
VC	11.8	FCC
NbC	13.4	FCC
ZrC	15.4	FCC
UC	18.3	FCC
UC ₂	23.2	Body centered tetragonal
U ₂ C ₃	39.8	BCC
U	12.4	
Ta	10.9	BCC
TaC	12.7	FCC
Ta ₂ C	25.7	HCP

Material	Percent Volume Increase Upon Conversion of Metal to Carbide	F_f° , 298°K Me _x Cy (k cal - mol ⁻¹) Per C Atom
Mo ₂ C	21.8	-4.93
MoC	35.1	-2.0
TiC	31.0	-43
VC	40.5	-27.5
NbC	25.2	-29.6
ZrC	38.6	-35.5
UC	47.0	-41 $\pm$ 10
UC ₂	87.1	-21
U ₂ C ₃	60.5	-25
TaC	16.5	-36
Ta ₂ C	17.9	-38

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III. GRAPHITE DEVELOPMENT

A. GRAPHITE

The primary objective of this investigation was development of a homogeneous graphite-fuel dispersion capable of approximately 12 atom % U-235 burnup using approximately 10 wt% fully enriched UO_2 or UC as fuel.

Satisfactory fission product retention is possible in standard fueled graphite only if large fuel particles are utilized. (18) Therefore, two approaches were initiated to the problem of maintaining integral fuel particles in graphite:

1) Investigation of standard graphites as matrices for refractory carbide-coated fuels.

2) Investigation of low temperature baked carbon (the graphite base material) as a matrix for ceramic coated fuels not chemically compatible with carbon at standard graphitization temperatures.

Several investigators have measured the physical and mechanical properties of a number of standard, or fully graphitized, graphite grades. These data have been compiled from the literature (Appendix A, Section 1). It is believed that, within limits, the behavior of a fully graphitized graphite can be predicted. It was decided, therefore, to devote the major experimental effort of this project toward exploration of the variations with temperature of physical and mechanical properties of a composite baked carbon-graphite body. Survey of the literature has shown that such measurements have not been made on this type of material.

The basic reason for interest in this material is its low processing temperature during manufacture ($760^{\circ}C$). This should greatly simplify retention of the geometric stability of fuel particle dispersions.

Standard graphites are generally processed at 2500°C or above. At these temperatures it is virtually impossible to retain original fuel particle dispersion without agglomeration or smearing of the fuel throughout the entire matrix.

The important properties evaluated in selection of a commercial graphite for use as a fuel matrix were:

- 1) Thermal expansion, particularly the ratio of expansions in the directions parallel and perpendicular to the grain.
- 2) Freedom from high cross-section impurities.
- 3) Thermal conductivity.
- 4) Mechanical properties such as tensile strength and Young's modulus.
- 5) Density.
- 6) The ability of the graphite to sustain an oxidation resistant coating

The graphites selected were Grade A and its modifications, produced by Great Lakes Carbon Co., Graphite Specialty Corporation's Grade W, and Grades H and O-15 manufactured by Speer Carbon Co.

Grade A, and variations, and W, high density types, approaching isotropic graphite have been fully graphitized at about 2500°C during manufacture. Accordingly, strength and thermal conductivity will be in the same range as those of similar standard graphites.

The ratios of thermal expansion measured in the direction parallel to the grain to expansions measured in the perpendicular to the grain are of great interest, since the graphite must support an oxidation resistant coating. It is known that coating performance is affected by anisotropy of thermal expansion in graphite although the magnitude of the effect is not known.* **

Speer Grade H is a molded material and Grade O-15 is extruded. Both grades utilize the same starting materials. The final firing temperature is much below that at which uranium, coated with either Al_2O_3 or BeO , will begin to react with carbon. (See Section I - FUEL).

Little was known about the thermal conductivity of Grade H and O-15 graphites at the operational temperature of the core. Ductility at room temperature was known to be lower than that of standard graphite. However, the rate of change of conductivity with temperature

* Personal communication, Minnesota Mining and Manufacturing Co.

** Personal communication, Dr. J. L. Kane, University of California Lawrence Radiation Laboratory.

was not known; data on thermal conductivity at high temperatures were not available. Therefore, experiments were undertaken to determine the thermal expansion, thermal conductivity and mechanical strength of the selected grades.

B. EXPERIMENTAL PROCEDURES

1. Mechanical Properties

Tensile strength determinations and stress-strain curves were made at various temperatures for grades H, O-15 and ATJ. Measurements were made with an Instron tensile testing machine with a specially designed furnace, capable of heating the sample to 2480°C in helium atmosphere. The furnace uses graphite resistor elements to heat the sample by radiation. Strain measurements are made by optical methods. Stress is measured in the usual manner. This equipment has been described in previous publications.⁽¹⁹⁾

The room temperature tensile strength determinations for grade AX-2 were made with standard tensile samples on a Baldwin-Universal testing machine.

2. Thermal Expansion

High temperature thermal expansion measurements were made for grades H and O-15, with the equipment described above. The thermal expansion coefficients for grades H, O-15, W, and A, from room temperature to approximately 1000°C were measured with a Leitz dilatometer.

3. Thermal Conductivity

The technique of Rasor et al.⁽²⁰⁾ was used for measuring thermal conductivity. A heat sink is placed at the center of a specimen to absorb energy coming through the specimen from an external heat source. The flow rate and the temperature rise of water in the heat sink provide a measure of the parameter q , or radial heat flow. All specimen temperatures were measured at the bottom of holes drilled into one end of the specimen. Optical pyrometry or thermocouples provided the necessary temperature information to determine the radial temperature drop ΔT , from edge to center of the specimen. Quantities a_1 and a_2 are the distances of the inner and outer sight holes from the axis respectively, and L is the length of specimen over which heat flow was measured (1 in. in this case). Using these data, thermal conductivity can be computed from the equation:

$$k = \frac{q \ln (a_2/a_1)}{2\pi L (\Delta T)}$$

(Equation 1)

Ends of the specimens were carefully insulated to reduce conductive heat loss. As an additional precaution, the portion of specimen over which the conductivity was measured was located approximately 1 in. from either end. Since the specimen temperature was uniform with the heat sink removed, it was necessary to make temperature corrections when it was in place. Consequently, an average of three temperature measurements taken at each position has been used.

C. EXPERIMENTAL RESULTS

1. Mechanical Properties Tests

According to data reported by others^(21, 22) and the present experimental tests, the tensile strength of graphite materials is an increasing function of temperature within the temperature range of interest.

The ultimate tensile strength as a function of temperature for each of the graphite grades tested at Aerojet, San Ramon, is shown in Figure 5. It should be noted that only ATJ samples were tested in both orientations. Grade H was tested only in the direction perpendicular to the grain and grade O-15 in the parallel direction. Tests were made in only one orientation because the sample material available did not permit machining test specimens in both orientations.

Tensile test data for grades H and O-15 are presented in Table 3.

Stress-strain curves for grades H and O-15 are shown in Figures 6 through 11. The measurements were made at various temperatures, with a constant strain rate.

Experimental limits of error for these determinations are $\pm 0.02\%$.

Experiments showed the ultimate tensile strength of grade AX-2 to be 2650 ± 50 psi at room temperature. The variation of strength of AX-2 with temperature was not measured. However, since it is a fully graphitized material it should follow a pattern more like that of ATJ than of grade H or O-15.

2. Thermal Expansion

Thermal expansion coefficients for grades H, O-15, A, AX-2 and W were measured over wide temperature ranges. The expansion coefficients for ATJ were obtained from the literature. The data are reported in Table 4, which also shows the ratio of the thermal expansion coefficient in the direction parallel to that in the direction perpendicular to the grain. This parameter is useful in estimating qualitatively the ability of graphite to sustain a surface coating when thermal cycled and for engineering design.

ULTIMATE STRENGTH vs TEMPERATURE FOR GRAPHITIC MATERIALS

TABLE 3ULTIMATE STRENGTH FOR GRAPHITESpeer Grade H Graphite
Cut Perpendicular to GrainSpeer 0-15 Graphite Cut
Parallel to Grain

<u>Temperature (°C)</u>	<u>Stress (psi)</u>	<u>Temperature (°C)</u>	<u>Stress (psi)</u>
20	3600	20	2225
20	3700	20	2370
760	4100	820	2350
760	4100	820	2350
1080	4650	1100	2675
1100	4100	1160	2500
1360	4350	1380	3100
1380	4050	1400	2500
1620	4580	1660	2950
1640	4500	1680	2900
1940	5200	1920	3450
1980	4100	1940	3850
2210	3600	2250	2630
2220	2800	2250	3900

STRESS-STRAIN MEASUREMENTS ON SPEER GRADE H GRAPHITE AT 1610°C AND 1635°C
CUT: PERPENDICULAR TO GRAIN
PLATEN RATE: 0.02 IN./MIN.

FIGURE 6

STRESS-STRAIN MEASUREMENTS ON SPEER GRADE H GRAPHITE AT 1935°C AND 1985°C
CUT: PERPENDICULAR TO GRAIN
PLATEN RATE: 0.02 IN./MIN

STRESS-STRAIN MEASUREMENTS ON SPEER GRADE H GRAPHITE AT 2210°C AND 2225°C

CUT: PERPENDICULAR TO GRAIN

PLATEN RATE = 0.02 IN./MIN

FIGURE 8
STRESS-STRAIN MEASUREMENTS ON SPEER GRADE 0-15 GRAPHITE AT 1660°C AND 1680°C

CUT: PARALLEL TO THE GRAIN

PLATEN RATE: 0.02 IN./MIN

FIGURE 9

STRESS-STRAIN MEASUREMENTS ON SPEER GRADE 0-15 GRAPHITE AT 1920°C AND 1935°C
CUT: PARALLEL TO THE GRAIN
PLATEN RATE: 0.02 IN./MIN

STRESS-STRAIN MEASUREMENTS ON SPEER GRADE 0-15 GRAPHITE AT 2250°C
CUT: PARALLEL TO THE GRAIN
PLATEN RATE: 0.02 IN./MIN

FIGURE 11

3. Thermal Conductivity

Thermal conductivity of an 0-15 graphite specimen was measured perpendicular to the grain. A piece of ATJ graphite was used for checking the equipment, but it was necessary to cut this specimen with the crystal orientation parallel to the direction along which thermal conductivity was to be measured. In one respect this was advantageous since there is a significant amount of data reported for thermal conductivity measured in this direction. The values derived agree fairly well with those of Rasor and Fieldhouse⁽²³⁾. Consequently it is felt that the data presented are accurate to approximately $\pm 5\%$. The experimental results are shown as a function of temperature in Figure 12 and tabulated in Table 5.

D. CONCLUSIONS

The ultimate tensile strength and stress-strain measurements have demonstrated that a composite graphite base material such as Speer grades H and 0-15 composed of graphite grains supported by a baked carbon binder possesses sufficient tensile strength and rigidity for use in the fuel element of the GCRE-II.

Thermal expansion measurements have shown that the fully graphitized graphites A and AX-2 and the baked carbon-graphite composite materials H and 0-15 are very nearly isotropic. However, the thermal expansions of H and 0-15 are higher than those of standard graphites. An isotropic material is more desirable from the viewpoint of core design because problems of differential thermal expansion are reduced. The effect of higher thermal expansion on design and also on coating performance remains to be evaluated.

The results of the thermal conductivity tests show the lower limiting case of difference in conductivity between a standard graphite and a baked carbon-graphite composite. The grade 0-15 data were measured perpendicular to the grain and the ATJ in the parallel direction. The direction in which the conductivity is measured is important; for a given graphite the conductivity measured parallel to the basal plane of the carbon atom layer structure will be greater than if measured in any other direction. Conversely, conductivity measured in the perpendicular direction will be lower than if measured in any other direction.

Thus it can reasonably be expected that the thermal conductivity of a composite material such as described here will, if measured in any other orientation, be equal to or higher than the measurements in the data presented here.

It is evident that a carbonaceous body composed of graphite grains and baked carbon grain boundaries is equal in mechanical properties to standard graphite for projected use as a fuel matrix in GCRE-II. The high temperature physical and mechanical properties of the materials when actually loaded with fuel have not yet been investigated. However, the demonstrated physical and mechanical properties of the material

indicate that further investigation is fully justified and that particular emphasis should be placed on thermal conductivity and fission product release. (See Section II, Fuels, for discussion of irradiation problems.)

TABLE 4

THERMAL EXPANSION COEFFICIENTS

Material	Linear Coefficient of Thermal Expansion		Temp. Range where Valid °C	Ratio CTE Para/CTE Perp.
	Parallel to Grain	Perpendicular to Grain		
Grade H	$6.43 \times 10^{-6}/^{\circ}\text{C}$	$6.72 \times 10^{-6}/^{\circ}\text{C}$	0-2200	0.95
Grade 0-15	6.24	7.01	0-2200	0.89
Grade W	4.22	2.83	0-1000	1.49
Grade ATJ(*)	4.60	5.37	0-1500	0.86
Grade ATJ(*)	5.75	9.92	0-2600	0.58
Grade A	5.10	5.10	0-550	1.00
Grade A	5.31	5.35	0-1050	0.94
Grade AX-2	4.94	5.30	0-550	0.93
Grade AX-2	5.18	5.57	0-1050	0.93

TABLE 5

MEASURED THERMAL CONDUCTIVITIES FOR ATJ AND 0-15

Thermal Conductivity - Btu/hr-ft-°F, $\pm 5\%$

<u>0-15, Perpendicular to Grain</u>	<u>ATJ, Parallel to Grain</u>	<u>Temperature °F</u>
54.0	56.0	700
43.5	45.0	1000
37.0	39.5	1200
31.5	33.5	1400
26.0	31.0	1600
22.0	27.5	1800
19.0	24.5	2000
17.0	22.0	2200
16.0	20.5	2400
15.0	19.5	2600
14.0	19.0	2800
13.0	18.5	3000
12.5	18.0	3200

*Armour Research Foundation, Progress Reports, Project ARF 6039-3.

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THERMAL CONDUCTIVITY OF ATJ AND O-15 GRAPHITES

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IV. DEVELOPMENT OF SILICON-SILICON CARBIDE COATING

A. OBJECTIVE

The corrosion effect of the reference GCRE-II coolant ($N_2 + \frac{1}{2}\% O_2$) on graphite at high temperatures is not known. It is assumed that graphite will remove the small amount of O_2 present. Therefore, development of oxidation-resistant coating for graphite was undertaken. An additional advantage of this coating is that it will permit operation of the reactor using atmospheric air as a coolant for short periods of time, in an emergency. Ultimately, it is hoped, the coating will be made sufficiently reliable to make possible a change of the reference coolant gas to atmospheric air for 10,000 hr operation at 1000°C.

A literature survey and contact with other workers in the field disclosed that the best coating developed, up to the present time, for the applications under investigation, is composed of silicon carbide containing excess silicon. Such coatings have been applied by two-step processes in which the silicon and silicon carbide are in distinctly separate layers of the coating, and by single step processes in which the silicon forms a matrix for a silicon carbide particle dispersion.

The two-step process was selected for these investigations and all experimental work has been confined to this approach.

B. MATERIALS

1. Graphite

Grades of graphite used for coating experiments are listed below:

<u>Grade</u>	<u>Manufacturer</u>	<u>Density gm/cc</u>	<u>CTE Ratio*</u>
ATJ	National Carbon Co.	1.71	0.86
A	Great Lakes Carbon Co.	1.92	0.99
AX-1	" " " "	1.67	--
AX-2	" " " "	1.69	0.93

*Ratio of the linear coefficient of thermal expansion in the direction parallel to the grain to that in the direction perpendicular to the grain both at room temperature.

Most of the experimental work was done with ATJ graphite because it was most easily available. However, this is not to be considered as an endorsement of the product.

2. Silicon

The silicon used was duPont Solar Cell grade. This was purchased in several different lots and the purity and grain size varied from batch to batch. The tabulation below gives the chemical analyses:

<u>Element</u>	<u>Batch 1</u>	<u>Batch 2</u>
Mg	None detected	0.0005%
Fe	0.003%	None detected
Cu	0.0003%	0.0005%
Zn	None detected	1.5%
Ca	None detected	None detected
Si	Principle	Principle
Pb	None detected	0.004%
	Total impurity: 33 ppm	Total impurity: 15,050 ppm

The coating produced by the second batch, which contained more zinc, was apparently the same as that produced by the first batch. It is possible that most of the zinc is volatilized during the heating cycles.

3. Slurrying Vehicles

Reagent grade acetone, VYNS resin and cyclohexanone were used as slurrying vehicles. The VYNS resin was purchased from the Bakelite Division of the Union Carbide Company. This material is 90 wt % vinyl chloride and 10 wt % vinyl acetate and has a specific gravity of 1.363. The cyclohexanone used was reagent grade.

C. EXPERIMENTAL PROCEDURES

1. Techniques

Two techniques were investigated for the application of a silicon-silicon carbide coating. Both are two-step processes in which a silicon carbide coating is applied to the graphite and then a silicon coating over the silicon carbide.

The coated graphite samples were evaluated for performance by an oxidation test at 1000°C and thermal cycling from 1000°C to approximately 400°C in 1 - 2 minutes in still air and reheating at about the same rate. These oxidation tests were conducted to the point of sample failure and were the prime criteria for determining coating acceptability.

The structure of the coating and the thickness and composition of the several coating layers were determined by metallographic and X-ray diffraction examination.

2. Application Furnace

A vacuum induction furnace was used for coating application. The power supply was a 450 kc, 2.5 kw Lepel high frequency generator. A cross sectional diagram of the vacuum enclosure is shown in Figure 13.

Vacuum was provided by a Welch Duoseal 5 cfm mechanical pump. A pyrex re-entrant trap was installed in the vacuum line just ahead of the pump to prevent any entrained ZrO₂ from entering the vacuum pump during the initial pump-down.

Pressure in the system was measured with a thermocouple vacuum gage. A Leeds and Northrup optical pyrometer was used for all temperature measurements.

3. Coating Processes

a. Outgassing of Graphite

All graphite samples were machined to nominal sample dimensions of 1 in. long by 0.75 in. dia and vacuum outgassed. Outgassing was done in the same furnace used for coating. The furnace was pumped down to about 3 microns and the sample was heated to approximately 1900°C, at which temperature the furnace pressure reached 650 microns. The furnace was then cooled and simultaneously backfilled with helium. The holding time at maximum temperature was necessarily short, not over two minutes. Although it is desirable to extend this holding time it was not possible with existing equipment.

b. Acetone Slurry Process

This process consists of two separate heating cycles. The first results in a silicon carbide coating directly on the

CROSS SECTION: COATING APPLICATION FURNACE AND VACUUM ENCLOSURE

graphite surface and the second in an elemental silicon coating on the silicon carbide coating.

Silicon metal powder (-100 to +200 mesh) was mixed with acetone to form a thick slurry. Agitation of the slurry was necessary to prevent the silicon powder from settling at the bottom.

The sample was painted with the slurry on all surfaces and allowed to dry for about an hour to evaporate most of the acetone. The sample was then placed in the furnace. Care was taken during placement because the silicon powder is easily knocked from the surface. The furnace chamber was evacuated to a pressure of about 3 microns and the heating cycle begun.

The firing cycle determines whether the coating is silicon or silicon carbide. When a silicon carbide coating is desired, the sample is heated in vacuum to about 1900°C where the pressure in the furnace is about 350 microns. For a silicon coating the heating is stopped at about 1650°C; here the pressure rises to about 200 microns. In both cases the furnace power is shut off at the desired terminal temperature and the furnace is then back-filled with helium and allowed to cool.

Results obtained with this coating process were not consistent. Some of the samples exhibited small lumps in the coating surface; others showed obvious thin spots in the coating surface, particularly at the slightly rounded corners. It is believed that these effects were the result of non-uniform temperature distribution during firing.

The crucible used in the experiments had a graphite lid and temperature was measured by an optical pyrometer focused on the bottom of a hole bored in the crucible lid. After considerable investigation it was determined that the temperature distribution in the sample was very sensitive to the position of the crucible with respect to the work coil and to the sample within the crucible. It was also found that the glow discharge in the furnace chamber interfered with accurate pyrometer readings and that the pyrometer filament picked up enough energy from the high frequency (450 kc) power source to cause discrepancies in the temperature readings.

On the basis of these findings optical pyrometry was abandoned. A new deeper crucible was designed with an open top (Figure 13) so that melting of the silicon could be observed visually. Good temperature uniformity was achieved with this procedure. Several significant observations were made as the silicon melted on the sample surface. It was noted that tiny droplets of molten silicon were popped or blown off of the sample surface on melting and the surface exhibited a two phase liquid mixture when the silicon melted. One appeared to be molten silicon and the other a slag-like liquid floating on the silicon. The molten silicon did not wet the surface of the graphite completely and would not flow evenly over the sample surface. This non-wetting

phenomenon occurred on both the silicon and silicon carbide firing cycles. Since it is well known that molten silicon easily wets silicon carbide and should wet graphite, it was decided that some unknown reaction between residue left by the acetone and the silicon was causing the problem. After several different binders were tried, the cyclohexanone-VYNS process was adopted.

c. Cyclohexanone-VYNS Process

This is a cementing process in which the silicon powder is bonded to the graphite surface previously coated with the binder.

The binder is a saturated solution of VYNS* resin in cyclohexanone at room temperature. The previously outgassed graphite sample was dipped in this solution to cover the surface completely. The excess binder was wiped off, leaving only a thin film on the sample surface. The sample was rolled in a shallow dish filled with -100 to +200 mesh silicon powder until the surface was covered liberally with the powder. The excess powder was brushed from the surface leaving only powder which was well bonded to the surface.

The deep open-top crucible shown in Figure 13 was used for firing. Optical pyrometry was not attempted. The "popping off" of molten silicon from the sample surface occurred to only a minor degree. No second phase was visible during melting and the molten silicon flowed over the sample surface smoothly. Very few lumps or irregularities were visible on the sample surface after cooling.

It was determined that a good silicon coating is produced if the furnace power is shut off approximately 25 seconds after melting begins. The time lapse allows the molten silicon to distribute itself over the sample surface. If the power is left on longer, silicon carbide will begin to form.

If a silicon carbide coating is desired, the power should not be shut off for at least 35 seconds after melting begins. In this case the power shutoff time is not critical since reaction to SiC is desired.

4. Oxidation Testing

Oxidation tests were conducted in a 3-in. ID Kanthal wound horizontal tube furnace at $1000 \pm 50^\circ\text{C}$ in still laboratory air. The coated samples were placed on a thin sheet of firebrick in the furnace hot zone. Both ends of the tube were plugged with insulating material to prevent temperature fluctuation resulting from air flow through the tube. The samples were removed at intervals, cooled and weighed and reinserted in the furnace.

*A mixture of 90 wt % vinyl chloride - 10 wt % vinyl acetate, commercially supplied by the Bakelite Division of Union Carbon Company.

Plots of weight vs square root of elapsed time for samples using the acetone process are shown in Figures 14 and 15. Samples coated when the optical pyrometer was used for temperature control are shown in Figure 14. About 90 samples were made by this process. Fifty per cent failed immediately or within the first 5 hr of testing. Another forty per cent failed within the first 100 hr of oxidation test and the remaining ten per cent failed before 500 hr elapsed. The samples represented in Figure 14 are the best ten per cent. Samples coated by the acetone process, in which the deeper, open-top crucible was used and visual operations made for temperature control, are shown in Figure 15. About 22 samples were made by this process and all but the four shown in Figure 15 failed in the first 5 hr of the oxidation test. In Figures 16 and 17, weight gain versus square root of elapsed oxidation time are shown for the first ten consecutive samples coated by the cyclohexanone process. Only one sample of the ten has failed. At this writing the remaining nine samples have completed over 3000 hr of oxidation test without further failure.

Data for two other batches of samples were made available just before publication of this report. One batch of ten samples and another of eight completed oxidation tests at 1000°C in laboratory air for 1000 hr and 1500 hr respectively. Weight gain vs square root of elapsed oxidation time for these samples are shown in Figures 16a and 17a.

5. Thermal Cycling

During the oxidation tests, the removal of the samples from the furnace and reheating at intervals furnished data on the effects of mild thermal cycling.

The samples were removed from the furnace with cold metal tongs, and allowed to cool in still laboratory air. Reheating followed the reverse process. Each sample was thermal cycled once each time the weight gain was checked during oxidation testing.

6. Metallography

Metallographic examinations were made of selected samples to determine the depth of SiC penetration into the graphite, the thickness of the Si and SiC coatings and the uniformity of coating thickness.

Average SiC coating penetrations with the acetone process are tabulated below:

DEPTH OF SiC PENETRATION (MILS)

<u>Graphite Type</u>	<u>Top</u>	<u>Sides</u>	<u>Bottom</u>
AX-1	160	70-90 non-uniform	70
AX-2	70	64-120 non-uniform	60
A	25-30	uniform all surfaces	
ATJ	40	uniform all surfaces	

Silicon coating thicknesses produced by the acetone process were less than one-half mil thick as determined by metallography.

The samples coated by the cyclohexanone process exhibited the same average penetrations as those tabulated above, but were much more uniform and showed thicker silicon coatings. Several specimens were mounted for examination and a selective chemical etching technique was used for qualitative determination of the silicon compounds present in the coating.

Following are the appropriate properties of the reagents used:*

<u>Acid</u>	<u>Property</u>
HF	Attacks SiO; will not attack Si ₂ C, SiC, Si
HNO ₃	Attacks Si ₂ C; will not attack Si, SiO ₂ , SiC
HF + HNO ₃	Attacks Si, SiO ₂ , Si ₂ C; will not attack SiC

These reagents were used in separate etching operations and the results were photomicrographed.

The sample selected for test was identified as Specimen 68, ATJ graphite coated with silicon-silicon carbide. This sample was oxidation tested at standard conditions for 24 hours and failed. The sample was cross sectioned and polished.

A picture of the specimen after this treatment is shown in Figure 18. The silicon outer coating is 5 ± 1 mils thick and the darker ring between the silicon coating and the plain graphite core is about .45 mils thick.

The sample was next oxidized at 1000°C for 4 min in a laboratory air furnace to remove some of the central graphite core. It was mounted in lucite and polished; the finished mount is shown in Figure 19.

* "Handbook of Chemistry and Physics" Chemical Rubber Publishing Co., Cleveland, Ohio.

WEIGHT GAIN OF S1-S1C COATED GRAPHITES
OXIDATION TESTED IN AIR, ATMOSPHERIC PRESS., 1000°C

FIGURE 14 ACETONE PROCESS
MELT. TEMP. CONTROL = PYROMETER READING

FIGURE 15 ACETONE PROCESS
MELT. TEMP. CONTROL = VISUAL

WEIGHT GAIN OF Si-SiC COATED A T J GRAPHITE
OXIDATION TESTED IN AIR AT ATMOSPHERIC PRESSURE AND 1000°C TEMPERATURE
CYCLOHEXANONE PROCESS

FIGURE 16A

FIGURE 17A

...ATJ graphite, coated with silicon-silicon carbide by
cyclohexanone process, as sectioned. **FIGURE 18**

...oxidized 4 min. at 1000°C, mounted and polished.

FIGURE 19

The outer layer seen in Figure 19 is obviously silicon with a few non-metallic inclusions and it appears to be well-bonded to the substrate coating. The silicon carbide coating is very thin with a single phase region about 1 mil thick. It appears much the same as the silicon layer in the photomicrographs and is located between the silicon layer and the much thicker composite silicon carbide-graphite layer which is characterized by large intrusions of silicon carbide in a graphite matrix.

There are many more inclusions in the thin continuous silicon carbide layer than in the silicon layer. The chemical etching procedure made possible the identification of most of these inclusions and showed a sharp line of demarcation between the silicon and silicon carbide layers.

The specimen after nitric acid etch is shown in Figure 20. Most of the small inclusions in the thin silicon carbide layer were dissolved by the acid as were many of the inclusions in the silicon carbide surrounded by graphite matrix.

The specimen is shown after hydrofluoric acid etch in Figure 21. There is obviously little difference between this and Figure 20 which shows the sample after nitric acid etch. It can be concluded that there are negligible, if any, amounts of silicon oxides present in the coating structure.

Specimen 68, after etching with a mixture of $\text{HF} + \text{HNO}_3$ for 60 sec, is shown in Figure 22. The outer layer of silicon was completely removed, leaving the thin continuous layer of SiC on the surface. The light areas in the photograph are SiC , the dark are graphite. The dark spots within the SiC formation are pits left by the dissolution of Si or Si_2C inclusions formerly in the SiC .

7. X-Ray Diffraction Examination

A Norelco diffractometer was used to examine the duPont silicon powder used in these investigations. A standard silicon powder for comparison, powder type #52131, serial #59-1048, was supplied by Norelco. The pattern from the duPont material was exactly the same as that from the Norelco standard, within limits of experimental error, with the exception of peak width at half maximum intensity. Comparable results were obtained from a check of the ASTM card file or X-ray diffraction data. The duPont silicon purchased by Aerojet had slightly wider peaks; however, this was expected since the material had not been annealed prior to X-ray examination.

Diffraction scans of the silicon coated surface of Sample 68, coated by the cyclohexanone process, showed SiC peaks and silicon peaks. The silicon peaks were of irregular intensities. This was expected because of the thinness of the silicon coating (4 mils) and consequent total penetration by the X-ray beam.

Specimen 68...

FIGURE 20

...etched with nitric acid.

FIGURE 21

...etched with hydrofluoric acid.

FIGURE 22

...etched with hydrofluoric acid
and nitric acid for 60 sec.

Diffraction patterns were made for the SiC coating on Sample 68. The patterns clearly show the presence of β SiC and graphite. Some of the α SiC peaks were present. No peaks corresponding to impurities or oxides (SiO, SiO₂) were present in the Si or SiC patterns.

D. CONCLUSIONS

Oxidation tests at 1000°C in air conclusively prove that the cyclohexanone-VYNS process is more reliable than the acetone process for production of silicon-silicon carbide coated graphite. The single failure of one of the ten samples coated by this process occurred at the midpoint of the cylindrical surface, where the metal tongs are clamped for removal of the sample from the oxidation furnace. The other nine samples were clamped in the same manner but did not fail; therefore it is probable that the failure resulted from rough handling and not thermal shock. The failure was not directly caused by oxidation.

The structure of the coating has been investigated by metallography and X-ray diffraction. It is tentatively identified as a 5 mil layer of SiC particles or islands (containing Si and Si₂C inclusions) dispersed in a graphite matrix proceeding inward from the air-silicon interface.

More statistical data are required to establish the reliability or failure rate of the cyclohexanone coating. More samples should be coated by the process and tested. It is suggested that Grade A graphite, which is a high density nuclear grade, be used in further coating work.

Further investigation is needed to determine if the cyclohexanone process coating can be applied to reimpregnated (higher density) baked carbon graphite composite material such as grades H and O-15, described in the graphite section of this report.

If further experimental work shows the cyclohexanone process to be statistically reliable, (i.e. if more than 75% of the samples are oxidation resistant for the required number of hours) construction of a larger coating furnace may be desirable. The best type is probably a horizontal high vacuum tube furnace using a graphite pipe as a resistor to heat the sample by radiation. This type of furnace should provide much greater uniformity and temperature control than does the induction furnace now in use.

A reliable non-destructive test should be developed to evaluate coating integrity.

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V. METAL CLADDING

Various materials that might serve as an interlayer between a graphite fuel body and outer unfueled can were considered as a part of this study. It became apparent that the material used would have to possess properties compatible with the graphite, be dimensionally stable and still retain fission products. Since the interlayer must also maintain a fair amount of ductility and strength, data on compatibility with graphite and effects from thermal cycling at a temperature of 1850°F became a primary requirement.

To evaluate various materials for these properties a literature search and an experimental program were initiated at Aerojet.

The materials selected for initial screening investigations were zirconium, Zircaloy-2, "A" nickel and K-Monel. Mechanical and physical property data compiled from the literature are presented in Appendix A. However, information in the literature was meager concerning properties of the selected materials at the required temperatures.

A. EXPERIMENTAL PROCEDURES

1. Compatibility Tests

Sealed capsules containing graphite and each of the selected materials in close contact were inserted into furnaces pressurized at 300 psi for 1000 and 1500 hr exposures at elevated temperatures.

The capsule assembly and test sample are shown in Figure 23. For each test a clean, flat metal specimen 2.0 in. x 1.4 in. x 0.050 in. was sandwiched between two solid half-cylinders of graphite and encapsulated. The graphite pieces were machined to provide good contact and outgassed at 1900°C in a vacuum of 10 microns prior to assembly. The test samples and capsules were assembled and welded closed in a glove box under

COMPATIBILITY TEST CAPSULE AND ASSEMBLY

a helium atmosphere. The capsules were helium leak-tested and found to be leak tight. The capsules were subjected to 300 psi external pressure to provide a good graphite-metal contact.

Test exposures are given in Table 6.

TABLE 6
EXPOSURES FOR GRAPHITE-METAL COMPATIBILITY TESTS

<u>No.</u>	<u>Metal</u>	<u>Time (hr)</u>	<u>Temperature (°F)</u>	<u>Pressure (psi)</u>
1.	Zirconium (Reactor grade)	1000	1750	300
2.	Zircaloy-2 (Reactor grade)	1000	1750	300
3.	Zirconium (Reactor grade)	1500	1850	300
4.	Zircaloy-2 (Reactor grade)	1500	1850	300
5.	Zirconium (Oxidized surface)	1500	1850	300
6.	Zirconium (Oxidized surface)	1500	1850	300
7.	"A" Nickel	1500	1850	300
8.	"A" Nickel	1500	1850	300
9.	K Monel	1500	1850	300
10.	K Monel	1500	1850	300

The capsules were again helium leak tested after exposure and no leaks were observed.

2. Thermal Cycling

To determine effects of thermal cycling on Zircaloy-2 tubing and to verify earlier information (Appendix A), specimens of tubing were thermal cycled 100 times from 850 to 1850°F in an inert atmosphere. The specimens tested were 3 in. long x 1 in. OD with a wall thickness of 0.048 in.

B. RESULTS

Visual examination of samples following the compatibility tests showed no gross changes in surface appearance after exposures. Selected sections taken from similar locations of

each of the test specimens of zirconium, Zircaloy-2, "A" nickel and K-Monel were compared with unexposed standard samples, by metallography, carbon chemistry and tensile tests, to determine whether carbon had diffused into the metal. Tensile tests were conducted on subsized samples 1.0 in. long, 0.250 in. wide and 0.025 - 0.050 in. thick at a maximum strain rate of 0.1 min. A comparison of the test data with standard properties is shown in Table 7.

1. Metallographic Examination

Metallographic examination of the zirconium and Zircaloy-2 samples after 1000 hr exposure at 1750°F showed no carburized case on either material. Similar samples, exposed at 1850°F for 1500 hr exhibited carburized cases of about 0.0015 in. and 0.0003 in. (average) thickness for zirconium and Zircaloy-2 respectively (Figures 24 and 25). The maximum case thicknesses were found to be 0.0023 in. for zirconium and 0.0006 in. for the Zircaloy-2. The zirconium samples prepared with oxidized surfaces exhibited carburized cases, after exposure, similar to those of the samples tested without the oxidized surface (Figure 26). Physical measurements showed that the zirconium with oxidized surfaces had the greatest case thickness, 0.0036 in., of all metal samples tested. The K-Monel and "A" nickel samples presented the best general appearance and showed no carburized cases after 1500 hr exposure at 1850°F.

2. Carbon Analysis

Each sample was subjected to carbon analysis which revealed that the carbon content of all samples increased in varying amounts. The greatest increase (0.74%) was observed in the zirconium samples prepared with oxidized surfaces, while the least increase was that in the K-Monel, which picked up a negligible amount of carbon. Results of carbon analyses for all the metals tested are compared to the carbon content of standard unexposed samples in Table 7.

3. Tensile Tests

The tensile and elongation values for all samples were obtained to determine what effects a carburized case or carbon diffusion would have on the metal properties. In Table 7 these values for the tested metals are compared with similar values for standard unexposed samples. Zirconium and Zircaloy showed the greatest loss in strength and ductility after test exposures of 1500 hr at 1850°F. The exposed zirconium samples with oxidized surfaces exhibited about 80% loss in elongation (ductility) and the exposed Zircaloy-2 sample showed about 30% loss in strength. The K Monel and "A" nickel samples exhibited an average loss of 7% and 13% in strength. The elongation of K Monel was increased by 18% and the "A" nickel showed a slight loss.

FIGURE 24 MAGNIFICATION 600X.
PHOTOMICROGRAPH OF ZIRCONIUM TEST SPEC-
IMEN AFTER 1500 HR. CONTACT AT 1850°F
WITH GRAPHITE. NOTE CARBURIZED CASE
(0.0015 IN AVERAGE).

FIGURE 25 MAGNIFICATION 300X.
PHOTOMICROGRAPH OF ZIRCALOY-2 TEST
SPECIMEN AFTER 1500 HR. CONTACT AT
1850°F WITH GRAPHITE. NOTE DISCON-
TINUOUS CARBURIZED CASE (0.0003 IN.
AVERAGE).

FIGURE 26 MAGNIFICATION 500X.
PHOTOMICROGRAPH OF ZIRCONIUM TEST SPEC-
IMEN (WITH OXIDIZED SURFACES) AFTER 1500
HR. CONTACT AT 1850°F WITH GRAPHITE. NOTE
CARBURIZED CASE (0.0015 IN. AVERAGE) CON-
TAINING SEVERAL VOIDS AND CRACKS.

TABLE -7- METAL COMPATIBILITY TEST DATA

Metal	Exposure (Hrs @ Temp °F)	Carbon (%)		Ultimate Strength (1000 psi)		ELONGATION (%)		Remarks
		A	B	A	B	A	B	
1. Zirconium	1000 @ 1750	0.04	0.09	70.0	70.2	44.0	8.0	Metallographic examination showed negligible carburization
2. Zircaloy-2	1000 @ 1750	0.01	0.06	101.0	89.8	28.0	22.0	Metallographic examination showed negligible carburization
3. Zirconium	1500 @ 1850	0.04	0.40	70.0	53.0	44.0	32.0	Carburization case observed 0.0015" ave 0.0023" max thickness
4. Zircaloy	1500 @ 1850	0.01	0.15	101.1	72.0	28.0	32.0	Carburization case observed 0.0003" ave -0.0006" max thickness
5. Zirconium (Oxid. surface)	1500 @ 1850	0.04	0.66	69.6	80.2	32.0	8.0	Carburization case observed 0.0015" ave 0.0036" max thickness
6. Zirconium (Oxid. surface)	1500 @ 1850	0.04	0.78	69.6	76.8	32.0	6.0	Carburization case observed 0.0010" ave 0.0013" max thickness
7. "A" Nickel	1500 @ 1850	0.05	0.21	67.2	55.3	37.0	36.0	Metallographic examination showed no carburization case or second phase carbon precipitation.
8. "A" Nickel	1500 @ 1850	0.05	0.18	69.2	64.3	37.0	36.0	Metallographic examination showed no carburization case, or second phase carbon precipitation.
9. "K" Monel	1500 @ 1850	0.16	0.17	99.4	89.3	44.0	52.0	Metallographic examination showed no carburization case, or second phase carbon precipitation.
10. "K" Monel	1500 @ 1850	0.16	0.18	99.4	95.5	44.0	52.0	Metallographic examination showed no carburization case, or second phase carbon precipitation.

Notes:

A = Standard sample properties without exposure

B = Sample properties after exposure

4. Thermal Cycling

Thermal cycling of Zircaloy-2 tubing from 850°F to 1850°F, 100 times, verified reports by others that the material will grow and form surface wrinkles. As shown in Figure 27, the samples grew 3.4% to 3.8% in length and exhibited wrinkled surfaces.

C. CONCLUSIONS

The K-Monel appears to possess the most desirable properties of the metals tested for use as an interlayer material between a graphite fuel body and an unfueled graphite can. From preliminary screening tests it appeared to be the material most compatible with graphite, possessing good strength and ductility and with negligible carburization or carbon diffusion after testing at 1850°F for 1500 hr.

The zirconium apparently possesses the least desirable properties of all metals tested for use as an interlayer material at 1850°F. Zirconium exhibited the largest carbon pickup (0.74%), the heaviest carburization case (0.0036 in.) and the greatest loss in ductility (85%) after testing for 1500 hr at 1850°F.

Thermal cycling of Zircaloy-2 between 850 and 1850°F caused the material to grow. This growth was accompanied by surface wrinkling.

Further tests conducted in the temperature ranges of 1850 to 2200°F should provide information of great value. Since carburization reactions are diffusion processes it is important that metal compatibility data be extended to longer times and higher temperatures. Reactor excursion temperatures must be accounted for in the material testing program because of the well known effects of temperature increase on diffusion controlled reaction rates.

FULL SCALE

ZIRCALOY TUBING BEFORE AND AFTER 100 THERMAL CYCLES
BETWEEN 850°F AND 1850°F. NOTE GROWTH AND WRINKLED
SURFACES OF CYCLED SAMPLES.

VI. CARBURIZATION BARRIERS

As previously indicated in this report, a fuel element concept utilizing a metal can for structural support as well as fission product retention was considered for applications where the maximum operational metal temperatures would not exceed 1750°F. Hastelloy X metal in this application appeared to possess strength and oxidation resistance at the design conditions. Consideration of Hastelloy X, however, meant that the metal also must be compatible with graphite or that a barrier material to prevent carburization must be provided.

The Haynes Stellite Company has reported that carburizing compounds in contact with Hastelloy X will carburize the metal at 1900°F. Experimental compatibility tests utilizing graphite in contact with Hastelloy X were conducted for 832 hr at 1750°F (300 psi). Chemical and metallographic examination showed that the carbon completely penetrated the 25 mil metal wall, increasing the carbon content by 0.43%. Representative photomicrographs of the standard Hastelloy X (0.10% carbon) and the exposed test sample (0.53% carbon) are shown in Figures 28 and 29.

Of several coating materials considered as possible carburization barriers, molybdenum, niobium carbide and zirconium carbide coatings on graphite were selected for screening tests.

The molybdenum coated specimens were supplied by Ethyl Corporation and the niobium carbide and zirconium carbide coated specimens by Battelle Memorial Institute.

Preliminary examination revealed that all sample coatings were gas permeable. The average thicknesses of the Mo, NbC and ZrC coatings were 0.002 in., 0.005 in., and 0.0015 in. respectively. Microstructural examinations indicated that the coatings were uniform in thickness with some irregularities due to the graphite surface. Photomicrographs of representative samples are shown in Figures 30, 31 and 32.

Figure 28. Photomicrograph of Hastelloy-X metal tube section unexposed. Note carbides throughout structure of reference material. (500 X).

Figure 29. Photomicrograph of Hastelloy-X metal tube section after exposure at 1750°C , in contact with graphite, for 832 hours. Note the heavy carbide concentration near contact surface and sizes of each throughout matrix. (500 X).

MOLYBDENUM COATING

GRAPHITE

MOLYBDENUM COATING ON GRAPHITE (0.002" THICK). MAGNIFICATION 250X

FIGURE 31. NIOBIUM CARBIDE COATING ON GRAPHITE. (0.005" THICK)
NOTE THE EXTENSIVE POROSITY THROUGHOUT THE COATING.
MAGNIFICATION 250X

FIGURE 32. ZIRCONIUM CARBIDE COATING ON GRAPHITE (0.0015" THICK)
NOTE THE POROSITY AND DISCONTINUITY OF THE COATING.
MAGNIFICATION 250X

A. COMPATIBILITY TESTS

Screening test specimens consisted of sealed Hastelloy X capsules each in contact with one of the coated graphite specimens in a helium atmosphere. These were exposed at temperatures of 1850°F and 1750°F inside furnaces pressurized at 300 psi with an atmosphere of $N_2 + \frac{1}{2}\% O_2$.

Tests were interrupted after 265 hours at 1850°F due to a furnace muffle rupture. The tests were resumed in another furnace operating at 1750°F with a pressure of 300 psi.

Exposure times and temperatures for each capsule are tabulated below:

Capsule No.	Coating	Time (hr)	Temperature °F
1	Molybdenum	265	1850
		1000	1750
2	Molybdenum	265	1850
		3000	1750
3	Niobium Carbide	265	1850
		1000	1750
4	Niobium Carbide	265	1850
		3000	1750
5	Zirconium Carbide	265	1850
		1000	1750

All capsules were leak tested following test exposures.

One capsule, containing the NbC coating and exposed for 1000 hr at 1750°F, was discarded when it was found to leak. Examination of this capsule and the sample indicated that portions of the graphite and NbC coating had reacted with the oxygen present in the corrosive atmosphere ($N_2 + \frac{1}{2}\% O_2$).

B. RESULTS

Examination of the coated graphite specimens in the remaining samples indicated that all coatings were unchanged. Microstructural examination disclosed no change in coating uniformity or thickness in any of the specimen coatings.

Portions of each Hastelloy X capsule were submitted for chemical analyses, tensile tests and metallographic examination. Tensile tests were conducted on sub-sized samples 1 in. long x 0.250 in. x 0.025 in. thick at a maximum strain rate of 0.1/min. Data obtained after testing are presented, in comparison with standard properties, in Tables 8 and 9.

1. Metallographic Examination

Metallographic examination of all Hastelloy X metal specimens contacting each of the coated graphites for 1000 and 3000 hr at 1750°F showed no carburized case or carbon pickup. The microstructures of each metal test specimen exposed for 3000 hr in contact with Mo, ZrC and NbC coated graphites appeared quite similar. Each specimen exhibited unusual second phase precipitates throughout the structure. Photomicrographs of representative Hastelloy X samples exposed in contact with the molybdenum coating are shown in Figures 33 and 34.

2. Carbon Analyses

Inside and outside sections of the wall, 50% of wall thickness, were taken from each Hastelloy X capsule and subjected to combustion analysis. The samples were taken from the same location on each capsule, and all interior sections had been in contact with the coated graphites. The analysis showed only a normal concentration of carbon; this indicated that there had been no carbon pickup during the tests. The test values are shown in Table 8.

3. Tensile Properties

The tensile and elongation values for all samples were obtained to determine the effect that carbon diffusion would have on the Hastelloy X metal if the coatings failed to function as carbon barriers. As shown in Table 8, no gross change was noted in strength. The elongation data, however, showed about 90% loss in ductility.

Since the sub-sized tensile samples used were quite small, results obtained do not appear representative of data taken from standard size tensile bars. A small reduced cross-section such as that which was tested (~ 0.007 in.²) over 1/2 in. gage length would produce a greater degree of error in comparison to standard test sizes. Notch sensitivity of the samples must also be considered since the outside surface of each capsule had been oxidized from the N₂ + 1/2% O₂ atmosphere present during the experiments.

C. CONCLUSIONS

Preliminary tests indicate that molybdenum, niobium carbide and zirconium carbide coatings on graphite are successful as carbon barriers to Hastelloy X at exposures of 1750°F for long time periods (3000 hr).

Further tests in the temperature range of 1850 to 2000°F will be required before firm conclusions can be drawn. The screening tests do not justify any final conclusions, since the loss in ductility of the various Hastelloy X specimens remains unexplained.

Figure 33. Photomicrograph of Hastelloy X metal tube section after exposure at 1750°F for 1000 hr. in contact with molybdenum coated graphite. Note the fine carbide dispersion and second phase precipitates throughout the matrix.

Figure 34. Photomicrograph of Hastelloy X metal tube section after exposure at 1750°F for 3000 hr. in contact with molybdenum coated graphite. Note similar carbides and second phase precipitates as shown in Figure 33.

TABLE 8 - HASTELLOY X TEST RESULTS

Barrier Material	Test Exposure		Carbon Pickup (%)	Tensile Strength (1000 psi)		Elongation %		Remarks on Exposed Samples
	Time (Hrs)	Temp (°F)		Standard	Exposed	Standard	Exposed	
1. None	832	1750	0.40	144.0	91.1	24.0	4.0	Metallographic examination showed carburized case of excess carbides throughout structure.
2. Molybdenum	265	1850	None	144.0	154.2	24.0	7.0	Metallographic examination showed no carburized case. Second phase noted.
	1000	1750						
3. Niobium Carbide	265	1850	-	-	-	-	-	Same as above
	1000	1750						
4. Zirconium Carbide	265	1850	None	-	99.6	-	1.0	Same as above
	3000	1750						
4. Zirconium Carbide	265	1850	None	-	115.0	-	0.5	Same as above
	3000	1750						

TABLE 9 - CHEMICAL COMPOSITION OF HASTELLOY X TEST SPECIMENS

HASTELLOY X SPECIMENS

No.	Coating Contact	Exposure (Hrs)	Fe	Mn	Si	Co	Mo	W	Zr	Cr	Ni	C
Typical	None	0	17.0	1.0*	1.0*	0.5	8.0	0.2	-	20.5	Bal	0.05
			20.0			2.0	10.0	1.0		23.0		0.15
1**	None	0	20.0	0.8	0.60	2.0	10.0	0.2	0.04	22.0	47.48	0.09
2	Molybdenum	1000	20.0	0.8	0.75	2.0	9.0	0.3	0.03	21.8	47.24	0.09
3	Molybdenum	3000	20.0	0.6	0.75	2.0	8.0	0.4	0.02	21.61	47.07	0.10
4	Niobium Carbide	3000	20.0	0.8	0.60	2.0	9.0	0.4	0.05	20.97	45.39	0.12
5	Zirconium	3000	20.0	0.8	0.60	2.0	9.0	0.2	0.05	23.0	43.06	0.09

* Maximum

** Reference stand (control) sample

VII. GRAPHITE JOINING

The joining of graphite parts constituted a problem in the fabrication of graphite fuel elements. According to design requirements, the graphite joints must be reliable and of good quality, possessing a minimum tensile strength of 1200 psi.

A brief test program was therefore initiated to evaluate the mechanical properties of two commercial graphite cements and binders and of various selected combinations utilizing furfuryl alcohol.

A. EXPERIMENTAL PROCEDURE

The samples fabricated for tensile testing consisted of cemented butt joints 3/8 in. diameter in the reduced sections. The cement fillers and binders used in joining the test samples were purchased from commercial vendors and mixed according to their recommendations. Also several non-recommended combinations using the filler and binding agents were made, applied and tested for comparison with the recommended mixes. The materials, processes and mixtures investigated are shown in Table 10.

The joint made by Process 1 (C-6 filler and binder) was fabricated by joining two short ATJ graphite rods 3/4 in. diameter x 3 in. long and machined to size with threaded ends for gripping.

In order to evaluate any effects produced by preparation of the joint surfaces the butt ends were prepared in both rough and smooth conditions prior to joining. Joint thicknesses were varied at 1/8 in., 1/16 in., and 1/32 in.

Cemented joints were pre-cured at 100°C for 4 hr in air and then at 125°C for 16 hr. Final curing temperatures of 400, 500, 600, and 700°C for 1 hr in argon atmosphere were used to determine the best temperature for the final cure.

TABLE -10- GRAPHITE CEMENT PROCESSES

Cement Process No.	Material	Mixture	Curing
1	C-6 filler powder C-6 liquid resin binder	100 gms C-6 filler + 18.5 gms C-6 binder	Pre-cured in air 4 hr @ 100°C, 16 hr @ 125°C Final in argon 1 hr @ 400, 500, 600, 700°C
2	Furfuryl alcohol Citric acid	9G v/o furfuryl alcohol + 5 v/o H ₂ O + 5 v/o citric acid heated @ 150°C	Pre-cured in air 12 hr @ 100°C Final cure 1 hr at 150°C
3	Furfuryl alcohol, Citric acid	90 v/o furfuryl alcohol + 5 v/o H ₂ O + 5 v/o citric acid	Pre-cured in air 12 hr @ 100°C Final cure 1 hr @ 150°C
4	C-6 filler, furfuryl alcohol, citric acid	15 gms C-6 filler + 10 cc Process No. 2 mixture	Pre-cured in air 12 hr @ 100°C Final cure 1 hr @ 150°C
5	C-6 filler, furfuryl alcohol, citric acid	25 gms C-6 filler + 10 cc Process No. 2 mixture	Pre-cured in air 12 hr @ 100°C Final cure 1 hr @ 150°C
6	Graphite powder, furfuryl alcohol, citric acid	20 gms C-6 filler + 10 cc Process No. 2 mixture	Pre-cured in air 12 hr @ 100°C Final cure 1 hr @ 150°C
7	C-6 filler, furfuryl alcohol, citric acid	10 gms C-6 filler + 10 cc Process No. 2 mixture	Pre-cured in air 12 hr @ 100°C Final cure 1 hr @ 150°C
8	#15 filler, fur- furyl alcohol, citric acid	10 gms #15 filler + 10 cc Process No. 2 mixture	Pre-cured in air 12 hr @ 100°C Final cure 1 hr @ 150°C
9	#15 filler #15 binder	100 gms #15 filler + 40 gms #15 binder	Pre-cured in air 12 hr @ 100°C Final cure 1 hr @ 150°C

Notes:

- Supplied by National Carbon Co. (proprietary composition)

Process 2 used a binder of furfuryl alcohol, water and citric acid. The joints were fabricated by the methods used in the first process, except for the curing process. The test samples were pre-cured at 100°C for 10 - 12 hr and cured at 150°C for 1 hr. All curing was done in air.

The remaining processes, 3 through 9, utilized various combinations of C-6, No. 15 and graphite fillers with furfuryl alcohol (Table 10). Test samples similar to those joined with the No. 1 mixture were fabricated. The curing temperatures used with Mixtures 3, 4, 5, 6 and 7 were the same as those used for Process 2. The final curing temperatures for Mixtures 8 and 9 were 500°C for 1 hr.

Mixes used in joint fabrication were applied on bare graphite surfaces or on surfaces impregnated with Mixture 3.

The tensile tests were conducted on samples having threaded ends with one end attached to a dynamometer scale and the other attached to a dead weight load. Two of the fractured tensile bars are shown in Figure 35.

B. RESULTS

A total of 114 tensile samples was tested. Test results are summarized in Table 11.

The cement and joining process showing the highest tensile strength was Process 7; in this process a combination of C-6 filler and furfuryl alcohol binder was applied to a rough surface previously impregnated with a mixture of furfuryl alcohol and citric acid. The maximum strength obtained was 2000 psi. The second and third highest tensile strengths were obtained from samples joined by Processes 8 and 4; the sample joints ruptured at 1800 and 1500 psi respectively.

The first process, a combination of C-6 filler and binder, produced the lowest rupture strength of all samples tested. The maximum strength obtained with this process was 250 psi.

C. CONCLUSIONS

Joint strengths of 1200 psi or better were achieved with the following cement process and materials:

- a. Cement Process No. 5 - (C-6 filler, furfuryl alcohol, citric acid)
- b. Cement Process No. 8 - (#15 filler, furfuryl alcohol, citric acid)
- c. Cement Process No. 4 - (C-6 filler, furfuryl alcohol, citric acid)
- d. Cement Process No. 9 - (#15 filler, #15 binder)

Joints made with Process 7 utilizing a combination of C-6 filler and furfuryl alcohol binder produced tensile strengths to 2000 psi.

TABLE 11 - TENSILE STRENGTHS OF GRAPHITE CEMENTS

<u>Cement Process No.</u>	<u>Number of Specimens</u>	<u>Tensile Strength (Max, psi)</u>
1	24 ^(a)	250
	30 ^(b)	300
	8 ^(c)	310
2	2 ^(d)	550
3	2 ^(e)	-
4	2	600
	2 ^(d)	1500
5	3	850
	6 ^(d)	1300
	2	500
	3 ^(d)	700
7	3	1400
	3 ^(d)	2000
8	16 ^(d)	1800
9	8 ^(d)	1400

Notes:

a = Joint thickness of 1/8 in.

b = Joint thickness of 1/16 in.

c = Joint thickness of 1/32 in.

d = Joint surfaces were pre-impregnated with Mixture No. 3

e = Failed to form joint

SCALE: FULL

GRAPHITE TENSILE BARS CEMENTED WITH C-6 FILLER AND POLYMERIZED FURFURYL ALCOHOL BINDER. MEASURED BREAKING STRESS WAS 2000 PSI. NOTE THE COARSE GRAIN IN THE CEMENTED SECTION WHERE FRACTURE OCCURRED.

Pre-impregnation of graphite surfaces with furfuryl alcohol (Mixture 3) improved the joint strengths.

Variation in curing temperatures between 400 and 700°C did not make an appreciable difference in joint strength.

Joint thickness of 1/16" or less with rough surface preparations improved the joint strength.

Since the screening data may contain errors due to test sample alignment, it is believed that further development and test work should be conducted.

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APPENDIX A

Basic Materials Technology

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APPENDIX A
BASIC MATERIALS TECHNOLOGY

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I. GRAPHITE

A. INTRODUCTION

Graphite, which is an allotropic form of carbon, has been used extensively as a nuclear reactor material. Stronger at high temperatures than most substances, graphite is unsurpassed in its resistance to heat and thermal shock. Its low density and high thermal conductivity largely compensate for its relatively low strength at lower temperatures. These properties, combined with ease in machining and ready availability, suggest the use of graphite in the construction of heat engines.

Synthetic graphite is superior in strength and purity to natural graphite. However, as an engineering material, synthetic graphite possesses a serious deficiency. In a single small sample of synthetic graphite, variations in structure and properties may exist; in larger pieces the existence of such variations is a certainty. No two pieces of graphite are precisely alike in structure or engineering properties. This is due largely to slight, uncontrolled variations in production parameters such as raw materials, particle size, forming method and coking and graphitizing heating cycles.

Common grades produced for nuclear applications are C.S., AGOT, GBF, TSF, produced by National Carbon Co., "A", produced by Great Lakes Carbon Co., "W" produced by Graphite Specialties; and 9018 produced by Speer Carbon Co.

Since many grades of graphite are available, the following discussion and data are devoted to graphites having small grain size and high strength (ATJ, A, AGOT, CSE).

B. ANISOTROPY

Anisotropy in the finished product is a function of fabrication method and particle shape of the raw material. It cannot be completely eliminated in a true graphite. When coke is crushed it splinters in such a way that one dimension is larger than the other two. This effect is most pronounced in the smaller size fractions. Effect in the final product is an "against the grain" and "with the grain" variation in physical properties. For extrusion, "with the grain" is parallel to the extrusion direction. For molding, "with the grain" is perpendicular to the direction of molding pressure. In general, the extruded bodies are about twice as anisotropic as the molded ones.

C. PROPERTIES

The physical and mechanical properties of graphite are discussed under each category and include both temperature and irradiation effects. It should be noted that the data on irradiation effects are reported for grades AGOT, and CSF, since material was not available for grades A or ATJ.

1. PHYSICAL PROPERTIES

a. Crystallography

The generally accepted structure of graphite is hexagonal with lattice spacing of 1.42 Å. The atoms are in parallel plane layers spaced 3.36 Å apart; the layers are displaced in their planes so that the center of each hexagon has, directly above and directly below it, a carbon atom of an adjacent layer. In this configuration one hexagon is directly above another hexagon in every third plane. The lattice constants for the generally accepted structure are: $a = 2.456\text{Å}$, $c_0 = 6.697\text{Å}$, bond angle = 120° .

b. Physical Constants⁽¹⁾⁽²⁾

The physical constants of graphite at room temperature are shown in Table A-1.

c. Density (Bulk)⁽²⁾

Bulk density is reported in grams/cubic centimeter and is determined by measurement of volume and weight. For various grades the density at room temperature can vary from 1.5 to 2.0 gm/cc. As shown in Figure A-1 the bulk density for graphites decreases about 10% with increasing temperature from 32° to 2192°F .

d. Thermal Conductivity⁽¹⁾

The thermal conductivity at elevated temperatures ($1022\text{--}4000^\circ\text{F}$) of ATJ graphite has been measured and reported in Table A-1. As shown in Figure A-2, the conductivity decreases with increasing

TABLE A-1

PHYSICAL PROPERTIES OF GRAPHITE

Atomic Wt	Melting Pt (°F)	Boiling Pt (°F)	Density g/cc	Elect Resistivity ⁽¹⁾ cm		Coeff of Thermal ⁽²⁾ Exp. 10 ⁻⁷ °F	
				a	b	a	b
12.01	Sublimes	Sublimes	1.50-2.0	40-50	35-45	13.0	19.2
Thermal Conductivity ⁽²⁾ Btu/hr ft-°F		Specific Ht. ^(*) Btu/#°F	Ht of Vaporization Kcal/mole	Ht. of Sublimation Kcal/mole		Thermal Neutron Cross- Section barns ⁻³ /atm	
a	b						
53.2	72.5	0.172	143	140-170		4.8	

ELEVATED TEMPERATURE PROPERTIES

Mean Coefficient of Thermal Expansion ⁽¹⁾ 10-7/ $^{\circ}$ F			Thermal Conductivity ⁽²⁾ Btu/hr-ft- $^{\circ}$ F		Specific Ht ^(*) Btu/# $^{\circ}$ F	
	<u>a</u>	<u>b</u>				
(77-4352 $^{\circ}$ F)	50-55.5	44.5-50.0	1022 $^{\circ}$ F		77 $^{\circ}$ F	0.172
(572-1492 $^{\circ}$ F)	38.9-33.39	33.3-38.9	2000 $^{\circ}$ F	21.0	260 $^{\circ}$ F	0.238
			2156 $^{\circ}$ F		622 $^{\circ}$ F	0.335
			2900 $^{\circ}$ F		982 $^{\circ}$ F	0.396
			3000 $^{\circ}$ F	18.9	1342 $^{\circ}$ F	0.428
			4000 $^{\circ}$ F	17.9	1702 $^{\circ}$ F	0.452
					2061 $^{\circ}$ F	0.473

Notes:

- a. Parallel to grain
b. Perpendicular to grain

1. Grade "A" graphite
2. Grade ATJ graphite
3. Grade AGOT graphite

* Private communication; Great Lakes Carbon Company

BULK DENSITY VS TEMPERATURE FOR GRAPHITE

FIGURE A-1

THERMAL CONDUCTIVITY VS TEMPERATURE FOR ATJ GRAPHITE (MOLDED)

temperature from 42.1 at 1022°F to 17.9 Btu/hr-ft-°F at 4000°F. The data plotted in Figure A-2 are a measure of conductivity both parallel and perpendicular to the grain. It has been reported that neutron radiation decreases magnitude of the thermal conductivity and also decreases the temperature dependence of thermal conductivity. In Figure A-3, it is shown that irradiation tends to remove the sharpness of the maximum as well as reduce the magnitude of thermal conductivity for irradiated AGOT graphite.

The damage to graphite resulting from irradiation at temperatures less than 100°C can be removed by annealing. If the exposure is less than 1200 Mwd/t the damage may be reduced more than half by heating to 300°C; while if the exposure is more than 1200 Mwd/t, the damage may be reduced somewhat less than half by heating to 600°C.

e. Specific Heat⁽¹⁾⁽²⁾

As shown in Figure A-4, the specific heat of graphite increases smoothly with temperature from 0.172 at 77°F to 0.473 Btu/°F at 2061°F. Irradiation produces an increase in the specific heat when measured at a temperature lower than the temperature of irradiation so that none of the damage has been removed by annealing. (See Figure A-5).

f. Dimensional Stability⁽¹⁾

When graphite is irradiated, the crystal lattice is distorted by carbon atoms which have been displaced from their normal sites by collisions with energetic particles, generally fast neutrons and the recoil carbon atoms. This distortion in the crystal lattice becomes apparent in a bulk graphite sample as a volume increase, or, in samples with preferred orientations, as an expansion in the c-direction (perpendicular to the base plane). The change in the lattice c-spacing may be measured by x-ray diffraction methods. In Figures A-6 and A-7 it can be seen that length and volume changes for AGOT grade graphite increased 25% and 4.5% respectively after irradiation exposures of 2500 Mwd/t at room temperatures. Other nuclear grades (for example CSF) exhibited slightly lower dimensional changes at similar irradiation exposures.

g. Thermal Expansion

The thermal expansion of crystalline graphite is extremely anisotropic and there appears to be no sound relationship between the crystal and bulk expansion. The data reported in Table A-1 chiefly concern the bulk expansion values.

h. Emissivity⁽⁴⁾

The emissivity of graphite has been reported to be between 0.75 and 0.90. It has been shown that emissivity values vary depending on the nature of the surface. It has been reported that prolonged heating at high temperatures will change the character of the surface and

THERMAL CONDUCTIVITY VS TEMPERATURE FOR IRRADIATED GRAPHITE (AGOT)

FIGURE A-3

SPECIFIC HEAT (C_p) VS TEMPERATURE FOR GRAPHITE (AGOT GRADE)

FIGURE A-4

SPECIFIC HEAT VS TEMPERATURE FOR IRRADIATED AND UNIRRADIATED GRAPHITE

FIGURE A-5

CHANGE OF LENGTH IN GRAPHITE AFTER IRRADIATION

CHANGE OF LENGTH (AGAINST GRAIN) VS IRRADIATION

CHANGE OF LENGTH (WITH GRAIN) VS IRRADIATION

FIGURE A-6

CHANGE OF VOLUME VS IRRADIATION FOR GRAPHITE

FIGURE A-7

increase the emissivity from 0.77 to 0.905. Figure A-8 shows emissivity as a function of temperature as measured by several investigators.

i. Refraction and Absorption of Light in Graphite⁽⁶⁾

The following expression determines the radiant energy refracted or absorbed in massive graphite: $J_x = J_o \exp (-4 \pi n K x / \lambda_o)$

Where: J_x, J_o = Intensity of parallel light at two planes within the graphite, the planes being perpendicular to the direction of propagation of the light and separated by a distance x .

n = Index of refraction for normal incidence.

K = Index of absorption for normal incidence in the direction of x and λ to be expressed in microns.

λ	n	K
0.436	1.90	0.36
0.492	1.94	0.34
0.546	1.96	0.34
0.578	1.97	0.33
0.623	2.00	0.33

k. Reflectivity of Graphite (Normal Incidence on Massive Graphite)⁽⁷⁾

The following data gives the ratio of reflected to incident light normal to the surface of massive graphite where:

$R_o = (100) J_r/J_i$

J_r = Intensity of reflected light

J_i = Intensity of incident light

λ = Wave length of incident light (microns)

λ	R_o	λ	R_o
0.20	18	1.60	32.0
0.25	19	2.00	35.2
0.30	19	2.50	39.5
0.35	19	3.00	43.0
0.40	21	3.50	46.0
0.50	22.5	4.00	47.5
0.60	23.5	5.00	50.5
0.70	24.0	6.00	52.0
0.80	25.0	7.00	53.5
1.00	26.8	8.00	55.5
1.20	28.3	9.00	57.5
1.40	30.0	10.00	59.0

TOTAL EMISSIVITY OF GRAPHITE AS DETERMINED BY VARIOUS INVESTIGATORS

FIGURE A-8

2. MECHANICAL PROPERTIES

a. Tensile and Compressive Strength⁽¹⁾⁽²⁾

The strength of graphite increases as the temperature increases, reaching a maximum at approximately 2500°C (4532°F). Figure A-9 shows the percent increase in tensile strength as a function of temperature for a typical graphite. The average tensile strength has been reported for molded grade ATJ at elevated temperatures (32-4532°F). In Table A-2, and Figure A-10, it is shown that the tensile strength increases from 2200 psi at 32°F to 3900 psi at 4000°F. The strength of graphite is increased by irradiation, attaining a maximum at an irradiation exposure of 70 to 200 Mwd/t (megawatt day/ton of uranium = 6.46×10^{17} nvt) gradually declining as the irradiation exposure increases beyond the range. The effects of irradiation on compressive strength of AGOT graphite are shown in Figure A-11.

b. Flexural Strength⁽¹⁾

The maximum fiber stress that grade ATJ graphite withstands before rupture in bending at elevated temperatures is shown in Table A-2. The data are plotted in Figure A-13 and show that strength increases markedly with increasing temperature from 400 psi at 32°F to 6300 psi at 3632°F.

c. Young's Modulus⁽¹⁾

The modulus for grade ATJ graphite at room temperature is shown in Table A-2. The effect of irradiation on this property produces an increase to a broad maximum at 150 Mwd/t and then a slight decrease to a saturation level.

Irradiation damage to graphite can be removed by thermal annealing. The degree of recovery for a particular property depends on the amount and temperature of irradiation exposure, annealing time and temperature and specific properties of the graphite. In Figure A-12, the change in Young's modulus has been plotted at several annealing temperatures. It can be seen that the largest part of recovery was achieved at a temperature of 215°C.

d. Impact⁽¹⁾

The impact strength at room temperature for grade ATJ graphite is reported in Table A-2.

e. Hardness⁽¹⁾

The average Rockwell hardness at room temperatures of grade ATJ graphite taken across the grain has been reported to be (R) 90. "R" values signify the use of a 1/2 inch ball and a 60 kilogram major load. (It should be noted that this hardness determination is of significance only for a fine grain graphite such as ATJ).

PERCENT INCREASE IN TENSILE STRENGTH FOR A
TYPICAL GRAPHITE AS A FUNCTION OF TEMPERATURE

FIGURE A-9

TABLE A-2

MECHANICAL PROPERTIES OF GRAPHITE GRADE (ATJ)

Temperature °F	Tensile Strength (psi)		Compressive Strength (psi)		Flexural Strength (psi)	Youngs Modulus (10 ⁵ /lbs/in ²)		Impact Strength (ft-lbs)	
	<u>a</u>	<u>b</u>	<u>a</u>	<u>b</u>	<u>b</u>	<u>a</u>	<u>b</u>	<u>a</u>	<u>b</u>
32	2200	2450			4000				
68	- -	- -	8380	8530	- -	1.40	1.15	0.036	0.045
752	2300	2500			4000				
1472	2450	2650			4600				
2192	2650	2800			5000				
2912	2950	3050			5500				
3632	3350	3450			6300				
4352	4050	4400							

a. Parallel to grain

b. Perpendicular to grain

SHORT-TIME TENSILE STRENGTH VS TEMPERATURE FOR A T J. MOLDED GRAPHITE

FIGURE A-10

MECHANICAL STRENGTHS OF AGOT-KC VS IRRADIATION

FIGURE A-11

ISOTHERMAL ANNEALING OF YOUNGS MODULUS (CSF GRAPHITE).
EXPOSURE: 670 MWD/T.

FIGURE A-12

FLEXURAL STRENGTH* VS TEMPERATURE FOR GRAPHITE (ATJ GRADE)

Hardness of graphite has been found to increase with irradiation reaching a saturation at 146 Mwd/t. At high irradiation levels (above 1200 Mwd/t) the hardness decreases.

f. Creep Properties⁽⁴⁾

Although graphite is considered a brittle material it begins to show an appreciable creep above 2000°C (3632°F). At 2500°C, graphite (grade ECA) elongations of 3% and 5.2% were reported after 1 and 2 hours respectively under a stress of 4500 psi.

g. Elastic and Plastic Elongation⁽⁴⁾

Poisson's ratio for graphite varies from 0.20 to 0.33. The average value is about 0.25. An indication of graphite (AGOT and C-18) ductility at a temperature of 4800°F is represented by reported elongations of 7 to 18% under tensile stress of ~400 psi.

3. RADIATION EFFECTS (GENERAL)

In a high temperature reactor core large amounts of gamma and fast neutron damage should not be a problem;⁽¹⁰⁾ continuous annealing at the core operational temperature will remove most of this damage as it occurs. However, fission fragment damage to the matrix persists at high temperatures. This has been verified by inpile thermal conductivity measurements.

Hunter's⁽¹¹⁾ theoretical calculations concerning radiation damage as a function of fuel particle size have been experimentally verified. Standard cold-molded graphite specimens containing UO₂ nodules of 4 different sizes were irradiated for 4 weeks at 180°F in the X-10 reactor at Oak Ridge National Laboratory. Kernohan⁽¹²⁾ tabulated the changes in thermal and electrical resistivity after irradiation.

<u>Approximate UO₂ Nodule Size - Microns</u>	<u>Increase in Resistivity (average of 3 determinations) Percent of Pre-Irradiation Values</u>	
	<u>Electrical</u>	<u>Thermal</u>
No UO ₂	27.5	11
586	21.2	9
334	21.1	13
94	28.1	13
16	83.0	50

Kernohan also studied the effect of annealing radiation damage in the above mentioned samples after irradiation.

Figure A-14 shows results of the annealing experiments on the electrical resistivity increase during irradiation. With coarse fuel nodules the effect of fission fragment plus fast neutron damage is approximately equal to fast neutron damage only in nonfueled graphite. The major part of damage in the 16 micron nodule fuel dispersion is due to fission fragments, not fast neutrons.

Figure A-15 illustrates the results of inpile thermal conductivity measurements as a function of irradiation temperature. This graphite is fueled with less than 5 micron diameter particles of mixed UC, UC₂ and UO₂ by impregnation with uranyl nitrate and firing. Thus the irradiation damage in all samples is identical and the curve illustrates only the effect of irradiation temperature.

RADIATION DAMAGE ANNEALING
UO₂-GRAPHITE BODIES

FIGURE A-14

INPILE THERMAL CONDUCTIVITY MEASUREMENTS FOR URANIUM IMPREGNATED GRAPHITE

FIGURE A-15

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II. ZIRCALOY-2

A. INTRODUCTION

Zircaloy-2 is an alloy of zirconium developed specifically for nuclear applications. It consists of about 1.5 wt% Sn, 0.12 wt% Fe, 0.05 wt% Ni, 0.10 wt% Cr, and the balance Zr. Characteristics which have made this material suitable for nuclear applications include: low absorption cross-sections for thermal neutrons and compatibility with uranium refractories as well as other physical properties.

Zircaloy-2 is easy to weld, but must be protected in controlled inert atmosphere boxes or by use of inert gas shields because of rapid rate of contamination with oxygen and nitrogen when welded in air.

Zircaloy-2 is easily fabricated. Products such as wire produced from rod drawing, sheet produced from rolling operations, tubes produced from extrusions, and a variety of parts produced by other methods have been made successfully to specified tolerances.

B. PROPERTIES

The mechanical and physical properties of Zircaloy-2 are discussed under each subject and include the temperature effects.

1. Mechanical Properties

a. Ultimate, Yield and Elongation

The ultimate and yield strengths of Zircaloy-2 decrease with increasing temperature as shown in Table A-3 and Figure A-16. From reported test results the ultimate and yield strengths of annealed material decreases from 71,000 and 43,500 psi at room temperature to 13,200 and 6,400 psi at 1200°F respectively. The percent elongation increases

TABLE A-3
Mechanical Properties^(a) of Zircaloy-2

Temperature °F	(1,2,3) Ultimate Strength (psi)	(1,2,3) 0.2% Yield Strength (psi)	(1,2,3) Elongation (%)	(2,4) Youngs Modulus (10 ⁶ lbs/in ²)	(1) Impact Strength (ft-lbs)	(5) Poissons Ratio
68	71,000	43,500	26.0	13.9	20	0.425
200	59,000	39,000	28.0		22	
300	49,000	31,000	31.0	13.3		0.383
400	41,000	25,000	34.0		60	
500	36,200	18,000	36.0			
600	31,000	17,000	38.0	11.4		
700	26,600	13,700	39.0			
1050	19,500	10,700	64.8	8.9		
1200	13,200	6,400	80.0	4.7		

Fatigue Results⁽¹⁾ at 600°F

Treatment	Endurance Limit psi (Unnotched)	Endurance Limit psi (Notched)	Fatigue (Ratio) ^b	Notch Sensitivity Index at 10 ⁸ Cycles ^c
Beta quenched & alpha annealed	27.5	11.0	0.80	0.60
Base annealed	28.0	9.0	0.87	0.85

Notes:

- Average value of annealed material
- Fatigue ratio = (Unnotched fatigue strength)/(Tensile strength)
- Notch sensitivity index $q = (K_q - 1)/(K_t - 1)$, K_f = unnotched/notched fatigue strength,
 K_t = (theoretical max stress at notch)/nominal stress

YIELD STRENGTH AND ULTIMATE STRENGTH VS TEMPERATURE FOR ZIRCALLOY-2

FIGURE A-16

with increase in temperature from 26.0% at room temperature to 80% at 1200°F (Table A-3 and Figure A-17).

b. Young's Modulus and Poisson's Ratio

The modulus of elasticity and Poisson's ratio have been reported at room temperatures of 68° to 1200°F and 69° to 300°F respectively. As shown in Table A-3 and Figure A-18 the modulus of elasticity decreases with increasing temperature from 13.9×10^6 psi at 1200°F.

c. Impact and Fatigue

Impact strength and fatigue data have been reported at elevated temperatures of 400°F and 600°F respectively. As shown in Table A-3 the impact strength increases from 20 at 68°F to 60 ft-lbs at 400°F. Some fatigue data (total strain versus cycles to failure) is shown in Figure A-19 for large and small samples tested at 68 and 550°F. Additional fatigue data is shown in Table A-3 for the endurance limit of notched and unnotched samples of different heat treatments.

d. Rupture and Creep Strength

The rupture and creep strength values at elevated temperatures are shown in Table A-4 and Figures A-20 and A-21 for annealed and cold work material. As shown in Figure A-20 the rupture strength decreases with increasing temperature from 27,700 psi and 65,500 psi at 304°F to 7,200 and 7,500 psi at 932°F for the annealed and cold worked Zircaloy respectively.

The creep strength of Zircaloy-2 is shown in Figure A-21 for a creep rate of 1% in 1000, 10,000, and 100,000 hours. As shown in Figure A-21 the creep stress required to produce a 1% creep ratio in 100,000 hours decreases with increasing temperature from 22,000 psi at 304°F to < 2,500 psi at 932°F for annealed material.

2. PHYSICAL PROPERTIES

The physical properties of Zircaloy-2 are shown in the attached Table A-5 and Figures A-22 and A-23.

a. Thermal Conductivity

The thermal conductivity vs temperature has been plotted in Figure A-23 from reported data presented in Table A-5. As shown in Figure A-23 thermal conductivity increases with increasing temperature from 6.8 at 69°F to 7.8 Btu/hr-ft°F at 932°F.

b. Thermal Expansion

The coefficient of thermal expansion for Zircaloy-2 in the alpha phase is reported in Table A-5. A typical thermal dialation

Table A-4

Creep and Stress Rupture of Zircaloy-2 at Elevated Temperatures

<u>Temperatures</u> <u>°F</u>	<u>Creep Stress⁽⁵⁾ For 1.0% In</u>			<u>Stress to Rupture⁽⁵⁾</u>
	<u>1000 Hrs</u> <u>(psi)</u>	<u>10,000 Hrs</u> <u>(psi)</u>	<u>100,000 Hrs</u> <u>(psi)</u>	<u>1000 Hrs</u> <u>(psi)</u>
304 annealed ^(a)	25,500	24,000	22,000	27,700
cold worked ^(a)	66,000	63,000	46,000	65,500
annealed ^(b)	29,000			35,000
446 annealed ^(a)	23,000	22,000	20,500	23,000
cold worked ^(a)	56,000	54,000	40,000	55,500
annealed ^(b)	26,000	25,500		26,000
653 annealed ^(a)	20,800	19,000	9,000	21,600
cold worked ^(a)	33,000	24,000	10,000	40,000
annealed ^(b)	20,300	19,000		21,000
797 annealed ^(a)	11,400	9,500	6,000	14,900
cold worked ^(a)	15,000	6,400	< 5,000	24,000
annealed ^(b)				16,000
932 annealed ^(a)	6,000	4,000	< 2,500	7,200
cold worked ^(a)	4,000	1,500	< 1,500	7,500
annealed ^(b)				9,000

(a) Average value of annealed and cold worked sheet material.

(b) Average values of annealed bar material.

Table A-5

Physical Properties of Zircaloy-2A. Chemical Composition⁽⁶⁾ (%)

<u>Sn</u>	<u>Fe</u>	<u>Cr</u>	<u>Ni</u>	<u>N</u>	<u>Zr</u>
1.2 - 1.7	0.07 - 0.20	0.05 - 0.15	0.03 - 0.08	0.01 Max	B±1

B. Density⁽²⁾ (gm/cm³)

6.55

C. Melting Range⁽⁷⁾ (°F)

3250 - 3350

D. Alpha-Beta Transformation Temperatures⁽²⁾ (°F)On heating: 1498 - 1526 ($\alpha/\alpha + \beta$); 1786 - 1824 ($\beta/\alpha + \beta$)On cooling: 1418 - 1445 ($\alpha/\alpha + \beta$); 1706 - 1760 ($\beta/\alpha + \beta$)E. Electrical Resistivity⁽²⁾ ($\mu\text{ohm} \cdot \text{cm}$)

70°F = 74

F. Thermal Conductivity⁽¹⁾ (Btu/hr ft. - °F)

at	$\frac{68^\circ\text{F}}{6.8}$	$\frac{212^\circ\text{F}}{6.9}$	$\frac{392^\circ\text{F}}{7.1}$	$\frac{572^\circ\text{F}}{7.4}$	$\frac{752^\circ\text{F}}{7.5}$	$\frac{932^\circ\text{F}}{7.8}$
----	--------------------------------	---------------------------------	---------------------------------	---------------------------------	---------------------------------	---------------------------------

G. Coefficient of Thermal Expansion⁽²⁾ ($10^{-6}/^\circ\text{F}$)

Alpha = 3.6/°F (68° to 1290°F)

H. Thermal - Neutron Absorption Cross-Section⁽¹⁾ (barns)

0.22 - 0.24

% ELONGATION VS TEMPERATURE FOR ZIRCALLOY-2

-106-

FIGURE A-17

MODULUS OF ELASTISITY VS TEMPERATURE FOR ZIRCALLOY -2

FIGURE A-13

TOTAL STRAIN % VS CYCLES TO FAILURE FOR ZIRCALOY -2

FIGURE A-19

RUPTURE STRENGTH VS TEMPERATURE AT 1000 hr FOR ZIRCALLOY-2

FIGURE A-20

CREEP STRENGTH VS TEMPERATURE FOR ZIRCALLOY -2

FIGURE A-21

THERMAL CONDUCTIVITY VS TEMPERATURE FOR ZIRCALLOY-2

TYPICAL THERMAL DILATION CURVE FOR ZIRCALOY-2

curve for Zircaloy-2 is shown in Figure A-23. It can be seen from the figure that the coefficients of thermal expansion for both heating and cooling cycles are equal at a temperature of approximately 1500°F. At this point the alpha-to-beta phase transformation begins. The irreversible change in unit length of the Zircaloy-2 between heating and cooling cycles, about 13×10^{-4} inch, is a result of the phase transformation and is partially dependent upon the degree of preferred orientation of the material. This effect can be minimized, but not eliminated, by using randomly oriented material.

c. Dimensional Stability ⁽⁶⁾

A property of Zircaloy-2 quite similar to zirconium is dimensional stability when thermally cycled. Zirconium has been noted to exhibit growth when cycled through the transformation range. In the case of pure zirconium, increases in length ranging from 2 to 0.05% per cycle have been observed by Bostrom (Westinghouse Corporation), the major part of the deformation occurring on cooling rather than on heating. The growth is less pronounced on the smaller beta grain size but seems to be unaffected by heating or cooling rate or temperatures above or below the transformation temperature. The growth is highly directional as observed for a very coarse beta grain size cycled through the transformation between 1050 and 750°C.

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III. NICKEL AND MONEL

A. INTRODUCTION

Nickel and its alloys are useful in reactor engineering principally as materials of construction. In comparison with many other materials, they are noted for high strength, and are among the strongest materials known for service at high temperatures. Nickel as used in commercially pure wrought form is known specifically as "A" - nickel.

Alloy elements such as copper, aluminum, iron, etc., are added to nickel to impart special properties. The mechanical and physical properties of "A" nickel and nickel-copper alloys (K-Monel, and L-C Monel) have been compiled and are discussed below.

K-Monel is an age hardenable alloy containing 29.5% Cu, 2.8% Al and 0.5% Ti. Strength and hardness, particularly in large sections, are comparable with those of heat treated alloy steels and in addition the alloy has good corrosion resistance to sulfuric acid and sea water. It is easily fabricated in the soft condition (140-180 Bhn) and is available as forgings, bars, rods, sheets, strips and wire, hot finished, cold drawn, annealed, and with various heat treatments.

L-C Monel is a Ni-Cu alloy containing about 13.5% copper and not hardenable by heat treatment. It has good corrosion resistance to both fresh, salt and potable waters containing appreciable amounts of CO₂. It is easily fabricated and available in various shapes as a commercial product.

B. PROPERTIES

1. Mechanical Properties

a. Ultimate, Yield and Elongation

The ultimate and yield strengths for K-Monel and "A"-nickel decrease with increasing temperature as shown in Tables A-6 and A-8, and Figure A-24. From reported data it is shown that the ultimate and yield strength of K-Monel is higher than the ultimate and yield strength of "A"-nickel at temperatures up to 1600°F. As shown in Figure A-24, the ultimate and yield strengths of annealed K-Monel decreases from 97,000 and 49,000 psi at room temperature to 63,000 and 44,000 psi at 1200°F

YIELD STRENGTH AND ULTIMATE STRENGTH VS TEMPERATURE FOR "A" NICKEL, K MONEL

FIGURE A-24

respectively. The ultimate and yield strengths of "A"-nickel decreases from 63,000 and 21,000 psi to 14,000 and 7,500 psi at 1400°F respectively. The percent elongation for K-Monel and nickel, as shown in Figure A-25, increases with increasing temperature from 44% and 51% at room temperature to 53% and 89% at 1400-1600°F for the respective materials.

b. Modulus of Elasticity and Poisson's Ratio

The modulus of elasticity for K-Monel and "A"-nickel have been reported at temperatures ranging from room temperature to 1400°F. As shown in Tables A-6 and A-8 and Figure A-26, the moduli of K-Monel and "A"-nickel decrease with increasing temperature from 26×10^6 psi and 30×10^6 psi at room temperature to 13×10^6 and 18×10^6 psi at 1200°F respectively. Poisson's ratio has been reported for both materials at room temperature in Tables A-6 and A-8.

c. Impact and Fatigue

The impact and fatigue strengths are reported for K-Monel and "A"-nickel in Tables A-6 and A-8 at room temperature.

d. Creep Strength

The creep strength values for K-Monel and "A"-nickel are shown in Tables A-6 and A-8, and Figure A-27. From the reported data it is shown that K-Monel has a higher creep strength than "A"-nickel. The creep stress required to produce 1% creep ratio in 10,000 hours for both materials is shown to decrease with increasing temperature. For K-Monel the stress decreases from 45,000 psi at 900°F to 9,500 psi at 1100°F, and for the "A"-nickel the stress decreases from 4,200 psi at 900°F to 2,400 psi at 1200°F.

2. Physical Properties

The physical properties of "A"-nickel and K-Monel are shown in the attached Tables A-7 and A-9, and Figure A-28.

a. Crystallography(1)

The crystal form of nickel is face-centered cubic. Although a close packed hexagonal structure has been reported for some nickel films, nickel is not considered to have allotropic forms. The matrices of the commercial nickel alloys are face-centered cubic in structure. The lattice constant, a , of high purity nickel is 3.5239 Å, while the closest approach of atoms is 2.491 Å. For wrought Monel, $a = 3.5481$ Å. The theoretical crystal (x-ray) density of nickel is 8.906 g/cm³.

b. Thermal Conductivity

The thermal conductivity for K-Monel and "A"-nickel is shown in Tables A-8 and A-9.

% ELONGATION VS TEMPERATURE FOR "A" NICKEL AND K-MONEL

FIGURE A-25

TABLE A-6

Mechanical Properties of K-Monel*

Temperature (°F)	(1,2,4)	(1,2,4)	(1,2,4)	(1,5)
	Ultimate Strength (psi)	0.2% Yield Strength (psi)	Elongation (%)	Hardness (R _B)
68	97,000	49,000	44.0	90
800	87,000	39,000	29.0	
1,200	63,000	44,000	- - -	
1,400	- - -	- - -	- - -	80
1,600	15,000	- - -	53.0	76
1,800	- - -	- - -	- - -	72

Temperature (°F)	(1,3)	(3)	Temperature (°F)	(1)**	(psi)
	Youngs Mod. (10 ⁶ psi)	Poissons Ratio		Creep Stress 10,000 Hrs	for 1% in 100,000 Hrs
68	26.0	0.36	750	- - -	67,000
212	26.0	0.40	800	- - -	48,000
392	25.8	0.43	900	45,000	25,000
572	25.0	0.45	1,000	21,000	8,500
752	22.0	0.38	1,100	9,500	- - -
932	17.7	- - -			
1,200	13.0	- - -			

(1)	(2)
Charpy Impact Strength (ft - lb)	Fatigue Strength 100,000,000 Cycles (psi)
170	38,500 - 45,500 psi

* Hot Rolled Material

** Cold Drawn, Age Hardened Material

TABLE A-7
Physical Properties of K-Monel

A. Chemical Composition⁽¹⁾

<u>C</u>	<u>Mn</u>	<u>Fe</u>	<u>Si</u>	<u>S</u>	<u>Cu</u>	<u>Al</u>	<u>Ni</u>
0.15	0.75	0.9	0.05	0.005	29.0	2.75	66.0

B. Density⁽¹⁾ (gm/cm³)

8.47

C. Melting Range⁽¹⁾⁽³⁾ (°F)

2400 - 2460

D. Electrical Resistivity⁽¹⁾ (ohm-cm)

68°F = 58.3

E. Thermal Conductivity⁽⁴⁾ (Btu/hr-ft-°F)

80 - 212°F = 10.8

F. Coefficient of Thermal Expansion⁽³⁾⁽⁴⁾ (10⁻⁶/°F)

at	<u>212°F</u>	<u>400°F</u>	<u>600°F</u>	<u>800°F</u>	<u>1000°F</u>	<u>1200°F</u>	<u>1400°F</u>
	7.8	7.9	8.3	8.7	9.1	9.5	9.9

G. Specific Heat⁽⁴⁾ (Btu/lb/°F)

70 - 750°F 0.127

H. Thermal Neutron Absorption Cross-Section⁽¹⁾

4.0 - 4.5 barns

TABLE A-8
Mechanical Properties of "A" Nickel

Temperature (°F)	(6) Ultimate Strength (psi)	Yield Strength (psi)	(6) Elongation (1%)	(6) Youngs Modulus (10 ⁶ psi)	(1,6) Creep Stress (psi) for 1% in	
					10,000 Hrs	100,000 Hrs
68	63,000	21,000	51	30.0		
600	61,500	19,500	54	29.0	52,000	23,500
700	54,000	18,000	61		19,000	8,800
800	43,500	16,500	64	26.0	7,800	3,700
900	37,000	15,500	66		4,200	
1,000	31,500	13,500	69	22.0	3,100	
1,200	21,500	10,000	76	18.0	2,400	
1,400	14,000	7,500	89	15.5		

(6) Poissons Ratio	(6) Fatigue Limit		(1) Charpy Impact Strength
	No Cycles	Stress (psi)	(ft - lbs)
0.31	10 ⁵	52,000	216
	10 ⁶	40,000	
	10 ⁷	34,000	
	10 ⁸	33,000	
	10 ⁹	33,000	

TABLE A-9

Physical Properties of "A" NickelA. Chemical Composition⁽⁴⁾ (%)

<u>C</u>	<u>Mn</u>	<u>Fe</u>	<u>Si</u>	<u>S</u>	<u>Cu</u>	<u>Ni</u>
0.06	0.25	0.15	0.05	0.005	0.05	99.45

B. Density⁽¹⁾ (gm/cm³)

8.89

C. Melting Range⁽⁴⁾ (°F)

2615 - 2635

D. Electrical Resistivity⁽¹⁾ (μ ohm-cm)

68°F = 9.5

E. Thermal Conductivity⁽¹⁾ Btu/hr-ft-°F)

at	$\frac{212^{\circ}\text{F}}{37.5}$	$\frac{392^{\circ}\text{F}}{33.7}$	$\frac{572^{\circ}\text{F}}{29.6}$	$\frac{752^{\circ}\text{F}}{27.2}$	$\frac{932^{\circ}\text{F}}{29.6}$	$\frac{1112^{\circ}\text{F}}{33.0}$
----	------------------------------------	------------------------------------	------------------------------------	------------------------------------	------------------------------------	-------------------------------------

F. Coefficient of Thermal Expansion⁽⁶⁾ (10⁻⁶/°F)

at	$\frac{68^{\circ}\text{F}}{4.7}$	$\frac{100^{\circ}\text{F}}{5.6}$	$\frac{200^{\circ}\text{F}}{7.0}$	$\frac{300^{\circ}\text{F}}{8.0}$	$\frac{400^{\circ}\text{F}}{8.5}$	$\frac{600^{\circ}\text{F}}{9.2}$	$\frac{800^{\circ}\text{F}}{9.5}$	$\frac{1000^{\circ}\text{F}}{9.7}$	$\frac{1200^{\circ}\text{F}}{9.7}$	$\frac{1400^{\circ}\text{F}}{9.7}$
----	----------------------------------	-----------------------------------	-----------------------------------	-----------------------------------	-----------------------------------	-----------------------------------	-----------------------------------	------------------------------------	------------------------------------	------------------------------------

G. Specific Heat (Btu/lb-°F)

80-212°F = 0.130

H. Thermal Neutron Absorption Cross Section⁽¹⁾

4.5 barns

MODULUS OF ELASTICITY VS TEMPERATURE FOR "A" NICKEL AND K-MONEL

FIGURE A-26

CREEP STRENGTH VS TEMPERATURE FOR "A" NICKEL, K-MONEL

FIGURE A-27

FIGURE A-28

At 212°F K-Monel has a value of 10.8 Btu/hr-ft-°F in comparison to 37.5 Btu/hr-ft-°F for "A"-nickel at the same temperature. With increasing temperature the conductivity of "A"-nickel decreases to 33.0 Btu/hr-ft-°F at 1112°F.

c. Thermal Expansion

The coefficients of thermal expansion for K-Monel and "A"-nickel are reported in Tables A-8 and A-9, and Figure A-28. As shown in Figure A-28, the curves for both materials appear to intersect at two temperatures indicating the same expansions at ~290°F and ~1300°F. It can also be seen that the expansion of "A"-nickel is greater than K-Monel between 290°F and 1300°F.

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