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WANL-TNR-114
PHASE 1

INITIAL SCREENING STUDIES
STUDY OF FUEL ADDITIVES
FOR ENHANCEMENT
OF FLIGHT SAFETY

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Foreword

The work described in this report is a result of the joint efforts of several organizations and their associated personnel.

M. F. Smith, J. M. Bzura, and G. H. Peterson carried out all the materials fabrication and processing in the Materials Department of the Astronuclear Laboratory. High temperature firing and sensitization heat treatments were conducted by L. Moberly at the Research Center.

E. F. Vandergrift and M. Dawida of the Materials Department performed a number of the room temperature tensile tests. R. Hewlett of the Research Center carried out the tensile and flexural strength tests at 2400°F. All the 4000°F tensile and flexural strength tests were conducted by F. J. Digesu of the Southern Research Institute in Birmingham, Alabama.

G. Rymer, C. R. Fritz, and M. E. Korposh of the Safeguards Engineering Division conducted all the screening oxidation tests on additive materials. E. A. Gulbransen and F. A. Brassart of the Research Center investigated the fundamental oxidation properties of the graphite-base materials. Metallography was performed by W. T. Harding of the Materials Department.

Abstract

An experimental program was conducted to determine effects of high melting point integral additives on the oxidation behavior and mechanical properties of unfueled and fueled NERVA reactor core materials. Mechanical property tests were conducted from room temperature to 4000°F and oxidation tests at 2200°F. A total of seventeen additives were investigated, comprising the carbides, nitrides, borides, and silicides of the refractory and reactive metals. Rhenium metal was also studied. Additives in amounts of 1 w/o and 5 w/o were incorporated in graphite matrix materials using the standard NERVA fuel element production procedures. Oxidation tests were conducted in a special flow system which simulated a high altitude re-entry trajectory point. Mechanical property tests consisted of tensile and flexural strength measurements carried out in argon or vacuum in suitable test facilities.

It was concluded that the most promising additives studied (WC, Mo₂C, VC, and Re) are capable of doubling the oxidation rate of unfueled and fueled NERVA core material with optimum concentrations. All additives increase the mechanical strength of normally processed core material over a wide temperature range if present in the optimum percentage. However, molybdenum carbide and rhenium were the only additives that appeared to increase the strength of fueled materials over the entire temperature range as measured by tensile and flexure tests. Sensitization (heating to 5000°F) produces significant lowering of mechanical strength of fueled and unfueled materials. Sensitization tends either to increase or decrease oxidation rates in fueled and unfueled materials, depending on the contained additive.

The work schedule for the second phase of the program is presented. WC, Mo₂C, VC, and Re were selected for further study of oxidation and mechanical properties. Some physical property data also will be obtained. Initial destruct tests will be conducted with emphasis on arc wind tunnel and chemical destruct behavior.

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Study of Fuel Additives for Enhancement of Flight Safety
Phase I: Initial Screening Studies

1. Introduction and Summary

The use of graphite and carbon in nuclear reactors for space propulsion systems has presented the problem of determining the safety hazard associated with the atmospheric re-entry of such reactors from orbit during controlled or random descent. Operation of the reactor during a space mission will produce highly radioactive fission products in the core. The core material, therefore, must be rendered harmless before descent to earth to preclude a toxic hazard being presented to the human population.

Several methods of destroying nuclear reactors before or during re-entry have been proposed. One procedure would involve reducing the reactor core to a multitude of small particles at high altitude which would burn up before ground impact due to re-entry aerodynamic heating and oxidation. It becomes of interest, therefore, to determine the oxidation burnup rates of small graphite particles under re-entry conditions, and to study means of further increasing these rates to enhance radioactive particle incineration in the upper atmosphere.

The Martin Company, in a study of nuclear rocket safety hazards conducted nearly two years ago,⁽¹⁾ had proposed that the use of certain integral additives in the reactor core might accelerate the oxidation burnup of small fueled graphite particles during atmospheric re-entry. This would occur subsequent to a primary destruct of the reactor during orbital degeneration which would be designed to reduce the massive core to very small particles. This thinking was based primarily on a theoretical analysis of the effect of oxidizable high melting point materials in causing an increase in the combustion rate of graphite base materials, either through a catalytic effect on the surface, complexing of combustion product molecules, or inherent greater oxidation tendencies of the additives themselves. It was believed that only small amounts of these additives would be necessary to significantly increase the oxidation rate of the basic fuel material without adversely

affecting its physical, mechanical or nuclear properties, or causing difficulty in fabrication and processing of fuel elements. Martin performed a few experimental oxidation runs on graphite-base materials containing additives using an arc plasma wind tunnel. No definitive quantitative data emerged but qualitatively it was determined that additives indeed could be used to enhance the oxidation rate of graphite in a re-entry situation. The question of further development effort on additives was not pursued because the contract work period ended before any program could be initiated.

When the Westinghouse Astronuclear Laboratory began work on the NERVA contract approximately two years ago, the flight safety aspects of missions involving the use of a nuclear reactor were studied in conjunction with the overall reactor design and test planning phases. Particularly, the problem of atmospheric re-entry of radioactive fuel particles as a function of particular flight conditions was subjected to close scrutiny. These studies were detailed in several reports issued by the Astronuclear Laboratory during the past year, in which definitive theoretical and experimental investigations were conducted on the behavior of small graphite particles which could re-enter after activation of some type of powerful primary engine destruct mechanism. (2) (3) (4)

The results of these studies indicated that fuel particles must be quite small as initially produced from destruct to guarantee complete burnup before ground impact. The small size required posed added problems to the already complex task of designing an adequate destruct system. Therefore, means were sought to provide some simple method of increasing re-entry burnup of graphite particles to permit the use of larger initial particle sizes and thereby lessen the problem of a satisfactory primary destruct design. Logically, the possibility of integral additives was raised again, and it was decided to conduct a modest program aimed at determination of the characteristics of available and suitable materials in the promotion of enhanced fuel oxidation.

The proposed program was divided into three major portions, to be conducted over a two year period. The first portion, initial screening studies and feasibility determination, was to be a six-month effort to evaluate in a reasonable manner all possible additive materials with a melting point above 4000°F. The second part of the program, also of

six months duration, was designed to study in more detail the most promising materials investigated in the screening studies to ascertain whether ultimate usefulness could be realized. The third phase of the program was to be a twelve month advanced development effort designed to provide information for eventual incorporation of additives into a prototype engine. This last phase would include the most advanced and expensive types of destruct capability tests and also would involve exposure of enriched fuel materials to operating reactor radiation environments. Consequently, only one or two superior additives developed in the earlier two portions of the program would be used in these investigations.

This report describes the results of the initial six month screening study program. A total of seventeen candidate additive materials were selected from an initial list of fifty-two compositions meeting the melting point criterion. These seventeen materials were incorporated in standard NERVA graphite fuel element mixtures, composed of both fueled and unfueled compositions, and were processed in a standard specified manner. Specimens of processed rod stock were subjected to mechanical property and oxidation tests over a wide range of temperatures, and performance of each additive was evaluated.

Analysis of the experimental results showed four additive materials to be definitely superior in performance from the standpoints of maintenance of mechanical integrity over a wide temperature range, coupled with significantly increased oxidation rates under simulated re-entry conditions. These four promising additives are tungsten carbide, molybdenum carbide, vanadium carbide and rhenium metal, incorporated in the basic graphite fuel mixture as 1-5 w/o additions of 2-3 micron diameter pure powders. These four additives were chosen as the materials for more detailed examination in the next six month program. This program will include more extensive oxidation and mechanical property tests as well as initiation of small scale destruct studies to determine material behavior under simulated environmental conditions.

2. Objectives of Program

The primary objective of the entire program was to develop a high temperature graphite-base nuclear fuel containing small quantities of integral additives, designed to enhance the re-entry burnup of reactor fragments or augment the operation of some primary destruct system. Primary destruct systems may take the form of explosives, thermochemical reactions, nuclear excursions, or combinations of one or more of these. The study concept was not restricted to a single possible destruct mechanism. Any means of reducing the probability of radioactive material surviving re-entry was considered. The purpose of placing integral additives in the NERVA fuel material is to accelerate the mechanical, thermal, or chemical destruction of the core by passive means, or to increase the rate at which core fragments are burned up during re-entry. The objective must be achieved without limiting the flight mission capability of the engine in any manner.

Additives may be effective in:

1. Enhancing mass loss rates of small particles during re-entry heating.
2. Increasing graphite fragmentation due to high explosive destruct.
3. Increasing the reaction between fueled graphite and a chemical reagent introduced to the core during destruct by an injection mechanism. This technique is termed thermochemical destruct.
4. Improving combined thermochemical and nuclear transient destruct.
5. Promoting the loss of fission products during high temperature cycling of the core.

In considering the goals of the additives program, it is important to be aware of the following restrictions on the selection of type and amount of additives:

1. The additive must be chemically compatible with the graphite fuel at elevated temperatures, both in the environment encountered in manufacturing processes and during reactor operation.
2. The additives must not have an adverse effect on the mechanical and thermal properties of the reactor core.

3. The additives must not have more than a small effect on the nuclear properties of the reactor. The tolerable loss of reactivity permissible in the core is subject to study not included in this report.
4. The additives must not present difficulties in the fabrication of fuel elements by standard procedures.

These restrictions must be applied within the concept of a two-fold approach to increasing fuel destruction: (1) inherent enhancement of destruct capability and (2) delayed sensitization of the fuel. The first approach refers to an additive which by its presence during or after reactor operation either increases re-entry oxidation or the fragmentation of the fuel by any of the previously mentioned primary destruct methods. The restriction that the additive must not adversely affect other important fuel properties presents a serious limitation to the application of this approach. The second possibility refers to the ability of an additive to demonstrate improved destruct capability by primary destruct techniques, but only after a specific abnormal reactor operating cycle. The abnormal cycle would generally produce a temperature above the normal operating temperature to permit "sensitization" of the fuel and consequent improvement of destruct action.

Taking all these factors into account, a technical program was formulated to provide a logical step-by-step development of the additive concept through an experimental evaluation. A certain amount of theoretical analysis was used at the beginning of the work to reduce a very large number of potential additive materials to a reasonable number which could be handled in a laboratory program. It will be seen that the additives chosen for test screening covered all basic types which realistically could be used in the present NERVA materials and design philosophy.

Six principal areas of activity are involved in the overall program, of which the first three formed the basic of the study reported here:

1. Theoretical analysis and evaluation
2. Fabrication of fuel containing additives
3. Initial screening studies
 - a) Dynamic oxidation studies (flowing air)

- b) Mechanical property tests (tensile and flexural strength)
- c) Thermal behavior (sensitization)
- d) Metallography
- 4. Destruct screening studies
 - a) Chemical destruct
 - b) Re-entry burnup
- 5. Materials evaluation
 - a) Physical properties (thermal conductivity, expansion, coefficient, x-ray)
 - b) Hydrogen corrosion
 - c) Coating studies
- 6. Final destruct and re-entry tests
 - a) Re-entry burnup
 - b) Explosive destruct
 - c) Nuclear transient
 - d) Fission product release

The following sections of the report discuss the theoretical analysis, fabrication of fuel and initial screening studies in detail. Based on the results of this evaluation, an outline is presented for conduct of the next six month phase of the development program.

3. Theoretical Analysis

In order to select a group of additive materials for experimental study, it was first necessary to define the environmental conditions in the reactor core under any normal operating procedure. By so doing, it was possible to eliminate obviously unsatisfactory additive materials at the very start of the program. For the purposes of this study, the reactor temperature requirement was selected as the prime initial criterion for selection. The maximum normal temperature of operation has been specified by Westinghouse design personnel as 4000°F, consistent with maximum power output of the present NERVA design. Consequently, since it is desirable that the melting or

dissociation point of any additive material be higher than the normal maximum operating temperature of the reactor under existing pressure conditions, a minimum of 4000°F melting point was set as the initial screening tool.

To meet the temperature requirement it is necessary to resort to certain refractory metals and to metal compounds such as the carbides, nitrides, borides, oxides, silicides, and sulfides of transition metals. A few intermetallic compounds with melting points above 4000°F can also be synthesized, but are not considered as suitable as the other more stable compounds mentioned. A listing of possible materials in the above categories is presented in Table I, which includes a number taken from the Martin Company report on nuclear rocket safety analysis. ⁽¹⁾

Obviously, it was impractical to conduct a reasonable screening analysis on all 52 materials listed in Table I, because of time and economic limitations in the program. Therefore, an attempt was made to select the most promising materials based on thermodynamic considerations, cost, and degree of similarity. For instance, only one candidate was chosen from some similar members of certain groups in the periodic table, since it was believed their behavior would be about the same. Also, it was thought that refractory oxides would be unsuitable, despite their high melting points, because of the reducing nature of the environment at high temperatures. The presence of excess carbon (and hydrogen) at operating temperatures would most likely result in some reduction of the oxides, with attendant undesirable release of gaseous products. Some elementary thermodynamics data was developed to support the viewpoint of oxide reduction at extremely high temperatures. Several compounds (Al_4C_3 , AlN , ThC_2) are not particularly stable at room temperature since they react with moisture in the atmosphere to form volatile reaction products. They were not considered attractive because of the handling and storage problem.

The reduced number of additives screened from the initial list are contained in Table II. These were selected on the basis of having the most favorable combination of properties as related to actual reactor operating conditions. It was on these materials that the detailed screening studies were conducted. It should be noted that the

Table I

Potential Additives Initially Considered*
 (Melting or Dissociation Point Above 4000°F)

Additive	Melting Point (°F)	Additive	Melting Point (°F)	Additive	Melting Point (°F)
W	6170	TiN	5800	TiB ₂	4900
Re	5755	ZrN	5400	ZrB ₂	5450
Os	4900	HfN	5990	HfB	5900
Ta	5425	Ta ₂ N	5590	NbB ₂	5400
Mo	4730			TaB ₂	5700
Nb	4474	ThN	4770	MoB	4100
Ir	4449			VB ₂	4450
Ru	4530	AlN	4350	WB	4350
		Be ₃ N ₄	4000		
TiC	5700			ThO ₂	5600
ZrC	6400	Zr ₃ Si ₂	4050	MgO	5070
HfC	7030	Zr ₆ Si ₅	4050	ZrO ₂	4900
VC	5100	TaSi ₂	4450	CeO ₂	4712
NbC	6330	WSi ₂	4000	CaO	4660
TaC	7020			BeO	4568
Mo ₂ C	4190	CeS	~4450	SrO	4406
WC	5200	ThS	~4100	Y ₂ O ₃	4380
ThC ₂	4810	BaS	~4100	Cr ₂ O ₃	4127
SiC	4000	HfS	~4000		
B ₄ C	>4000				
Al ₄ C ₃	4900				

Table II

Additives Used in Experimental Screening Studies

WC	B ₄ C	Ta ₂ N
Mo ₂ C	VC	ZrN
NbC	WB	TaSi ₂
ZrC	ZrB ₂	WSi ₂
TiC	TiB ₂	Re
TaC	NbB ₂	

four basic classes of materials used comprising the IV, V, and VI groups of transition metals compounded in the form of carbides, borides, nitrides, and silicides. Elemental rhenium also appeared attractive since it apparently does not form a stable carbide within the temperature ranges of interest.

It was decided to incorporate the additives in the basic graphite mixture in the form of fine powders (2-3 microns diameter) to assure uniform mixing and maximum distribution. Two levels of additions were used (1 w/o and 5 w/o) to include what would be considered a reasonable range for evaluation of the quantity effect on destruct enhancement, without exceeding an amount which would present problems in fabrication and processing of fuel element materials.

4. Experimental Procedure

The experimental procedure, in accordance with the objectives and technical approach previously discussed, consisted of the following basic steps:

- 1) Selection of fuel matrix materials, fuel particles, and additives for preparation of required test materials.
- 2) Fabrication and processing of representative specimens of materials containing various amounts and types of additives. To furnish bases of comparison, four distinct groups of materials were prepared in the same manner which contained (a) only the basic graphite matrix mixture, (b) the basic graphite matrix mixture with additive and no fuel, (c) the basic graphite matrix mixture with fuel and no additive, and (d) the basic graphite matrix mixture with both additive and fuel. Group (c) approximated the current base NERVA fuel with maximum uranium loading. Group (d) simulated the desired additive-containing fuel on which extensive engineering tests eventually would be run to determine suitability for use in reactor cores. Groups (a) and (b) were designed to supply parametric information on the independent effects of additives and fuel in the matrix, thereby furnishing additional data on the mechanisms of observed behavior.

- 3) Oxidation tests in flowing air atmospheres to determine the effects of additives in accelerating the burnup rate of fueled and unfueled materials. The oxidation apparatus was designed to simulate high altitude, high velocity re-entry along a typical small particle trajectory.
- 4) Mechanical property studies at room and elevated temperatures to determine the effects of additives on basic strength characteristics. For the initial screening studies, tensile strength and flexural strength measurements were considered to be the most applicable for graphite-base materials.
- 5) "Sensitization" treatment of representative materials to determine effects of additives on degradation of properties resulting from transient heating to temperatures far above normal operating temperatures.

4.A Materials

The raw materials used in the experimental investigations may be divided conveniently into three categories: (1) fuel element matrix materials, (2) fuel particles, and (3) additive materials. The characteristics of each will be presented briefly.

Fuel element matrix materials consisted of fine graphite flours, carbon black, and liquid carbonaceous binder. These high-purity materials are normally blended in the proportions set forth by NERVA fuel element manufacturing specifications. The proper percentage of uranium carbide fuel particles are also added to the initial dry mixture to provide the proper uranium density in the final product. The dry blending, addition of the liquid binder, two-phase blending, fabrication, curing, baking, and firing are sequential process steps carried out in a carefully controlled manner to produce finished fuel elements of proper geometry, composite density and distributed uranium content.

Fuel particles of uranium dicarbide (UC_2) were obtained from Minnesota Mining and Manufacturing Company. The particles were coated with pyrolytic carbon and were furnished in accordance with the current specification for fuel particles used in the manufacture of production elements. These particles contained depleted uranium rather than enriched uranium in order to avoid cumbersome criticality and accountability restrictions. It was believed the physical, mechanical, and chemical properties of the

depleted and enriched materials would be identical. The nuclear properties, of course, are different and in later tests which might involve behavior under irradiation or reactor transient conditions, it would be necessary to use the appropriately enriched material. For the screening studies reported here, no enriched uranium was incorporated in the test stock produced.

The additive materials consisted of high purity micron size particles of the desired chemical composition, added to the dry fuel element mixture and blended thoroughly prior to addition of the liquid binder. In the final product these additive particles appeared under the microscope as uniformly distributed particles in the grain boundaries of the graphite matrix. The additive particles are considerably smaller than the graphite flour particles, but are considerably larger than the particles of carbon black.

The additives chosen for the screening studies (Table II) were procured from several sources. Since the scale of laboratory operations for production of specimen material was small, and because the additive did not exceed 5 w/o of the final composition in any case, only small quantities of additives needed to be purchased for this phase of the program. Some pertinent information on the selected additives is shown in Table III.

4.B Material Fabrication and Processing

The experimental method applied to produce the materials for the test program was established to conform as closely as possible to the current graphite fuel element production procedures of the Westinghouse Atomic Fuel Department. These procedures are used in making full size fuel elements for the present design of NERVA reactor. The primary steps consist of mixing, extrusion, curing, baking, and firing. Since production of full-size elements in the WANL Materials Department was neither practical nor desirable, a scaled-down facility was installed to employ the same types of equipment as the large production facility, but of much more limited capacity. To accomplish the various steps of fabrication and processing, the following items of equipment were used:

Table III

Information on Additives Investigated in Program

<u>Composition</u>	<u>Supplier</u>	<u>Average Particle Size</u>	<u>Analysis (w/o)</u>	
ZrC	Firth-Sterling	3.10 microns	Total C	11.26
			Free C	.44
			Si	.02
			Cr	.003
			Co	.005
			Ni	.003
			B	.001
			Fe	.02
			Ti	.02
NbC	Firth-Sterling	2.20 microns	Total C	11.26
			Free C	.44
			Si, Mn, Co, Ni, Cu, Al, B, Mg, Bi, Ag, Ge, Be, W, Mo, Sb, Ti, Pb, Zr, Ba	<.001
				<.01
B ₄ C	Firth-Sterling	3.20 microns	B	77.00 min.
			B ₄ C	99.00 min.
			Fe	0.2 max.
TiC	Firth-Sterling	2.85 microns	Total C	19.40
			Free C	0.20
VC	Firth-Sterling	2-3 microns		
WC	Firth-Sterling	2-3 microns		
Mo ₂ C	Firth-Sterling	2-3 microns		

Table III (continued)

<u>Composition</u>	<u>Supplier</u>	<u>Average Particle Size</u>	<u>Analysis (w/o)</u>	
TaC	Firth-Sterling	2.40 microns	Total C	6.32
			Free C	.10
			Fe	.05
			Si	.10
			Cb	.05
			Ti	.006
WB	Borolite Corp.	-200 mesh	98.5 min. purity	
ZrB ₂	Borolite Corp.	-200 mesh	98.5 min. purity	
TiB ₂	Borolite Corp.	-200 mesh	98.5 min. purity	
NbB ₂	Borolite Corp.	-200 mesh	98.5 min. purity	
Ta ₂ N	Borolite Corp.	-200 mesh	98.5 min. purity	
ZrN	A. D. Mackay	-200 mesh	98.5 min. purity	
TaSi ₂	Borolite Corp.	-200 mesh	98.5 min. purity	
WSi ₂	Borolite Corp.	-200 mesh	98.5 min. purity	
Re	Var-Lac-Oid	-200 mesh	99.987 purity	

1. Loomis 37 1/2 ton vertical extrusion press
2. Patterson-Kelley 8 quart V-blender
3. Hobart chopping machine
4. Low-temperature circulating air oven (curing cycle)
5. Intermediate-temperature argon atmosphere electric muffle furnace (baking cycle)
6. High-temperature argon atmosphere induction furnace (firing cycle)

The dry graphite matrix ingredients, consisting of 85 w/o No. 1008 graphite flour (National Carbon Company) and 15 w/o Thermax were weighed and then dried in a vacuum oven at 200°C for approximately one hour. The purpose of the drying treatment was to remove layers of adsorbed water vapor on the surfaces of the graphite particles. After drying, the graphite mix was transferred to the Patterson-Kelley V-blender where additives or fuel particles were introduced. Mixing was carried out for 30 minutes to ensure that all components were thoroughly blended.

The liquid binder, consisting of Varcum (partially polymerized furfuryl alcohol) catalyzed with 4 grams of maleic anhydride per 100 cc of Varcum, was prepared immediately prior to its addition to the dry graphite mixture. The maleic anhydride was crushed to -20 mesh powder and added to the Varcum. The liquid was stirred for 10 minutes with an electric stirrer to facilitate solution of the powder.

Batches for extrusion and subsequent processing normally consisted of 2 lbs. of dry graphite ingredients plus varying amounts of additives. The quantity of binder used was calculated as follows:

$$B = 0.3 \left[\overline{DCI} + \left(\frac{\rho_{UO_2}}{\rho_{ADD}} \times 0.127 \times A \right) \right]$$

where B = weight of binder in grams

DCI = weight of dry carbon ingredients in grams

A = weight of additive in grams

$\frac{\rho_{UO_2}}{\rho_{ADD}}$ = ratio of UO₂ density to additive density

This formula evolved empirically, and was adopted after considerable difficulty was experienced in curing various extruded materials. It is not considered optimum, but only a workable compromise.

Addition of the binder to the dry mixture was then followed by manual mixing. This was accomplished by placing the dry materials in a bowl, adding the catalyzed binder and kneading for approximately 5 minutes. Rubber gloves were used to protect the hands. Additional blending was accomplished by passing the material through a Hobart chopper prior to extrusion. The chopper provides an action similar to that of a meat grinder, and thoroughly blends the damp mixture under pressure. During chopping, the temperature of the mix rose to 40-45°C and it was extruded at this warm temperature. The extruded material was then passed through the chopper again and re-extruded. The geometry of the extrusion press and the nature of the chopped extrusion mix were such that approximately one-third of the material fed into the press remained in the chamber after each extrusion was completed. In order to assure that all of the usable material was extruded at least twice, a total of three extrusions were made on each batch with two intermediate re-chopping steps.

Extrusion was carried out in a 75,000 lb. vertical Loomis extrusion press. The chamber diameter was 2 3/8", and the die had a nominal 3/8" diameter with a total included entrance angle of 120°. This corresponded to an area reduction ratio of approximately 40:1. Extrusion pressures were in the neighborhood of 9000 lbs. load on the 2 3/8" diameter ram. The chamber was evacuated by means of a mechanical pump after loading and prior to extrusion. The purpose of this step was to prevent air inclusion and blistering in the product. The final extrusion was made in multiple 12" lengths to facilitate loading of the materials in the curing furnace. To accomplish this, the ram was stopped and re-started after each 12" length was extruded. One chamber load of material normally yielded about 20 feet of extruded 3/8" diameter solid rod.

The extruded pieces were placed on 1/2" thick transite trays and cured in a Blue "M" circulating-air oven. Work was scheduled so that extrusion was completed near the end of the working day. The furnace was then held overnight at a temperature of 50°C.

The next morning the furnace temperature was raised from 50°C to 250°C, with 10-15°C increments every half hour. Upon reaching temperature, the power was cut off, the furnace door opened, and the material allowed to cool to room temperature.

The purpose of the cure process is to complete polymerization of the organic binder. The material is then subjected to a baking treatment to coke the polymerized binder and drive off volatile constituents. The 12-inch lengths of cured rods first were sectioned into 4-inch lengths to facilitate handling and improve gas evolution rate. The short lengths were placed in a Vycor tube at room temperature, approximately 40 pieces per load. The tube was then placed in a 6-foot long Hevi-Duty muffle furnace. The baking treatment was carried out in flowing argon. Furnace temperature was quickly raised to 250°C, the highest cure temperature. Heating rates of 50-75°C per hour were then used to bring the material up through the range 300-600°C. At this time large amounts of pungent smoke, water vapor, etc. were given off. Too rapid a heating rate in this range resulted in surface spalling on the pieces. Between 650-850°C, the evolution of volatiles diminished sharply and heating rates of 100°C per hour could be used for the remainder of the baking cycle. Furnace power was shut off at 850°C and material furnace-cooled in argon to 300°C, after which it was removed from the furnace.

The final step, firing or "graphitization," was also carried out in flowing argon. Between 40-45 specimens were placed in a graphite crucible. The material temperature was raised from ambient to 1900°C in approximately two hours and held at this temperature for six hours. After this treatment, the crucible and its contents were allowed to cool overnight in the furnace in an argon atmosphere.

Temperatures during the curing cycle were measured by a chromel-alumel thermocouple placed near the middle of the specimen tray. In the baking process the furnace, with its Inconel muffle and Vycor tube in place, was calibrated to determine the hot zone profile. Following this, a single thermocouple was placed in the center of the hot zone between the muffle and the Vycor tube to measure baking temperatures. The firing temperature was measured with a Leeds-Northrup optical pyrometer sighted through a black body sight port extending through the crucible and sample-holder walls.

The above steps completed the normal thermal treatment of fabricated material. For the special "sensitization" treatments, the baked material was placed in the firing furnace and raised to a temperature of 2750°C (5000°F) in a flowing argon atmosphere. With a normal load of material (40 pieces) this procedure required 2-3 hours for heating to temperature, and 4-5 hours for cooldown. This treatment was designed to simulate the effects of deliberate or accidental overheating of the core beyond the normal operating temperature of approximately 4000°F. As will be seen from subsequent discussions, the sensitization treatment produces marked effects on the properties of fueled and unfueled materials containing additives.

The success of the fabrication and processing treatments in producing material identical to that of the Westinghouse fuel element production facility can be determined to a great extent by comparison of the final fired density and composition of unfueled and fueled reference specimens containing no additives. Since additives are presently not used in the production of fuel elements, these two categories of material are the only ones available for comparison at the present time.

Table IV contains data on density measurements for all compositions produced in the initial screening study for test purposes. Densities were calculated from accurate measurements of the physical dimensions and weight of the specimens. At least three determinations were made on each composition and an average taken of these values. In all cases the individual measurements of density varied no more than 2%. The average densities of unfueled and fueled production material are included for comparison. It may be seen that the values are the same for unfueled stock and within 3% for the fueled stock. As will be discussed later, metallographic examination of representative materials containing fuel or additives shows a uniform dispersion of these particles throughout the graphite matrix. It may be stated that the small scale fabrication and processing techniques used in the study have been successful in providing finished materials essentially the same as those manufactured in the full-scale production facility. It would be logical, therefore, to assume that the behavior of the production materials would be very similar to that of the laboratory generated product under the same test conditions.

Table IV
Densities of Fired Materials Used in Screening Studies

<u>Composition</u> ⁽¹⁾	<u>Density (g/cc)</u>	
	<u>Unsensitized</u> ⁽²⁾	<u>Sensitized</u> ⁽³⁾
Unfueled Reference (WANL)	1.80	1.81
Unfueled Reference (WAFD)	1.82	--
Fueled Reference (WANL)	2.11	2.13
Fueled Reference (WAFD)	2.17	--
1 w/o WC	1.81	1.83
5 w/o WC	1.91	1.94
1 w/o Mo ₂ C	1.84	1.86
5 w/o Mo ₂ C	1.88	1.89
1 w/o NbC	1.81	1.84
5 w/o NbC	1.87	--
1 w/o ZrC	1.80	--
5 w/o ZrC	1.85	--
1 w/o TiC	1.80	
5 w/o TiC	1.88	
1 w/o TaC	1.83	--
5 w/o TaC	1.88	--

(1) Weight percentage is actual contained percentage of the metal constituent, rather than the compound.

(2) Fired at 1900°C for 6 hours in argon.

(3) Fired at 2750°C for 2 hours in argon.

Table IV (Continued)

Composition	Density (g/cc)	
	Unsensitized	Sensitized
1 w/o Re	1.83	--
1 w/o B ₄ C	1.81	--
5 w/o B ₄ C	1.83	--
1 w/o VC	1.84	--
5 w/o VC	1.90	--
1 w/o WB	1.83	--
5 w/o WB	1.91	--
1 w/o ZrB ₂	1.81	--
5 w/o ZrB ₂	1.89	--
1 w/o TiB ₂	1.83	--
5 w/o TiB ₂	1.83	--
1 w/o NbB ₂	1.87	--
5 w/o NbB ₂	1.89	--
1 w/o Ta ₂ N	1.83	--
5 w/o Ta ₂ N	1.89	--
1 w/o ZrN	1.82	--
5 w/o ZrN	1.84	--
1 w/o TaSi ₂	1.81	--
5 w/o TaSi ₂	1.85	--
1 w/o WSi ₂	1.82	--
5 w/o WSi ₂	1.88	--

4. C. Oxidation Screening Studies

A simple oxidation test was devised by G. Rymer to evaluate the effects of various additives on the oxidation rate of pure graphite and uranium-fueled graphite. The approach taken in the initial screening study phase of the program was to subject a wide variety of additive-bearing graphite materials to a standardized oxidation test. It was not of concern at this time to perform a fundamental kinetic study. Rather, it was the intention to develop a screening test by means of which it would be possible to obtain comparative rates of oxidation of graphites containing different types and amounts of additives.

4.C.1. Apparatus

A design of the test apparatus and the selection of operating parameters for the desired test conditions were determined by the following criteria:

- 1) The predicted environmental conditions to which a particle would be exposed during re-entry into the earth's atmosphere. Among the primary parameters would be surface temperature, pressure, and gas stream velocity.
- 2) The feasibility of achieving any or all of the necessary parametric conditions in one simple test apparatus.
- 3) The desirability of producing mild oxidation conditions in the apparatus to limit specimen degradation and thereby permit accumulation of valid differential rate data.

The conditions selected for specimen evaluation were a specimen temperature of 1200°C and a system pressure of 0.1 Torr. These conditions approximate the stagnation pressure and median temperature encountered by a 1/8" diameter spherical particle traveling at a velocity of Mach 5 at an altitude of 280,000 feet. It should be noted that only stagnation pressure and specimen temperature are simulated. The gas flow velocity in the apparatus was calculated to be approximately 1100 cm per second. Although this velocity is considerably below anticipated re-entry velocities, it was deemed sufficiently fast to provide comparative rate data within the scope of the standard test.

The specimens used for the oxidation studies were in the shape of small solid cylinders of 0.125-inch diameter and 0.132-inch length. A 0.013-inch hole was drilled through the diameter of each sample and a platinum suspension wire was passed through the hole to support the specimen in the furnace. Several specimens were prepared with different lengths and diameters to determine what effects the sample geometry might have on the reaction rate.

Kinetic oxidation studies were made in the reduced pressure flow system shown in Figure 1. Compressed air (Airco) was dried by passage through a magnesium perchlorate-silica gel drying tube (A). The dried air was admitted to the reaction tube (F) through a capillary in a flowmeter (E). In order to maintain a constant pressure drop across the flow meter, hence a constant flow rate of air, excess pressure at the flowmeter inlet was exhausted through a ballast bulb (B) and solenoid valve (C) to a rotary vacuum pump. The solenoid was actuated by a Thermocap relay which monitored the mercury height in the manometric leg (D) of the flowmeter.

Air entering the reaction tube was preheated by passage over a pebble bed of crushed "mullite". Effluent reaction gases were exhausted from the reaction tube by a mercury diffusion pump (H). A cold trap (G) served to prevent mercury vapor from back-streaming into the reaction tube. The reaction gases were vented to a rotary vacuum pump through a two-way stop cock (I) or were entrained to pre-evacuated sample bulbs (J) through a manifold (K). The reaction tube was heated by a Kanthal element resistance furnace (L) which was raised to the reaction tube position by a pulley and counterweight system.

Details of the reaction tube itself are shown in Figure 2. Specimens were suspended in the hot zone by means of an 8-mil platinum wire which was in turn suspended from a hook fastened to a pyrex cap. The hot zone consisted of a mullite tube of 1-inch diameter, packed to a depth of 6 inches with mullite chips. The mullite tube was fastened to a stainless steel head by an "O-ring" flange. A 1/4-inch diameter mullite gas delivery tube, attached to a 1/4-inch diameter stainless steel tube in the cold

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LOW PRESSURE FLOW SYSTEM

Figure 1

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- A. STAINLESS STEEL HEAD
- B. PRESSURE THERMOCOUPLE PLUG
- C. TEMPERATURE THERMOCOUPLE
- D. GAS INLET TUBE
- E. "O RING" FLANGE
- F. "MULLITE" TUBE
- G. PLATINUM SUSPENSION WIRE
- H. "MULLITE" PREHEAT BED

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REACTION TUBE

Figure 2

zone, extended to the bottom of the mullite preheat bed. Thermocouple temperature and pressure instrumentation ports were incorporated in the stainless steel head. A stainless steel-pyrex "O-ring" flange connected the reaction tube to the vacuum inlet.

The specimen temperature was determined with a calibrated Pt-Pt + 10% Rh thermocouple. The thermocouple output was directed across a Leeds and Northrup portable potentiometer and read on a 1-millivolt Leeds and Northrup recorder. Sample pressure was monitored on a Veeco thermocouple gauge which was standardized periodically with a mercury McLeod gauge.

Samples of the effluent gas from the reaction tube were taken in 1-liter pre-evacuated sample bottles. The gas samples, which were at 0.5-Torr pressure, were compressed to atmospheric pressure and introduced through a Toepler pump to a Fisher gas chromatograph.

4. C. 2 Procedure

A typical run consisted of weighing and suspending a specimen in the reaction tube. The tube was then evacuated to 10^{-5} Torr of mercury, and the specimen degassed at 1200°C for 30 minutes. Previous experiments had shown no significant weight loss during this treatment. Dried air was then admitted to the system for 10 minutes at a pressure of 0.1 Torr. After terminating the air flow, the furnace was lowered and the specimen allowed to cool to room temperature in vacuum. The specimen was then reweighed. This procedure was repeated at the same pressure and temperature for a 20 minute period.

Additional tests were made at various times and temperatures for the pure graphite and fueled graphite reference material. Also, samples of the effluent reaction gases were collected and analyzed.

4. C. 3 Calculations

In order to obtain differential rate data for graphite oxidation, it is desirable to determine the weight loss of graphite as a function of time. The time increments between measurements should be very small, or better still, provisions can be made to continuously record the weight change as a function of time during the run. It was found, however,

that under the experimental conditions of this program a plot of weight loss versus time was linear and extrapolated through the origin. This apparent zero order linear proportionality with time permitted the characterization of the reaction rate equation with fewer data points. For the majority of the tests, weight losses were determined at only two exposure times (10 and 20 minutes).

Using this technique, the reaction rate (dW/dt) in milligrams per minute could be obtained from the slope of a plot of weight loss in milligrams as a function of time in minutes. This rate may be converted to dn/dt , the reaction rate in atoms per minute, by the relationship:

$$dn/dt = dW/dt \times 10^{-3} \frac{N}{M} \text{ atoms/min}$$

where N = Avogadro's number

M = Molecular weight of carbon.

It is customary in computing rate data to normalize the rates to a per gram basis. It was found, however, that the rates were directly proportional to the geometric surface area in this study. Accordingly, the values obtained for dn/dt were divided by 0.55 cm^2 , the geometric surface area of the test specimens. One final correction is needed to account for the portion of the weight loss which is due to oxidation of the additive material. As a first approximation it was assumed that graphite and additive material oxidized at the same rate. Hence the specimen weight loss during the run could be normalized by the relative densities of reference graphite specimens to additive-containing specimens. The corrected rate expression then becomes:

$$dn/dt = dW/dt \times \frac{10^{-3}}{A} \frac{N}{M} \frac{d_1}{d_2} \text{ atoms/cm}^2\text{-min}$$

where A = specimen surface area (0.55 cm^2)

d_1 = density of reference graphite

d_2 = density of test specimen.

4. C. 4 Temperature Dependence

The reaction rate of the reference graphite material was found to obey the Arrhenius equation over the temperature range 800° - 1400°C. This equation has the form:

$$K = Ae^{\frac{-E}{RT}}$$

where $K = dn/dt$, the reaction rate

A = frequency factor

E = activation energy in cal/mole

R = gas constant

T = temperature in °K

It is apparent that the slope of a plot of $\log K$ versus $\frac{1}{T}$ will yield E . The activation energy determined in this manner was found to be 18.3 kilocalories per mole. This value indicates that, under the given experimental conditions, the graphite oxidation reaction is occurring in a regime intermediate between the chemical reaction controlled regime ($E = 39-45$ K cal/mol) and the diffusion controlled regime ($E = 0$.K cal/mol).

4. C. 5 The Oxidation Mechanism

Samples of the effluent gases analyzed by gas chromatography showed the principal oxidation product to be carbon monoxide. For this phase of the work only a qualitative analysis was performed. It is significant, however, that in no instance was carbon dioxide found.

If it is assumed that the oxidation mechanism is:

then it is possible to calculate the efficiency of the graphite-oxygen reaction. In all experiments the flow rate of air was 7.8 cc/min at standard temperature and pressure.

For a 20 minute run this would be:

$$7.8 \times 20 \times 0.2099 = 32.7 \text{ cc of } O_2$$

The moles of oxygen supplied were:

$$\frac{32.7}{22.4 \times 10^3} = 1.46 \times 10^{-3} \text{ moles of } O_2 \text{ or } 2.92 \times 10^{-3} \text{ moles of } O.$$

The weight of reference graphite lost in this 20 minute interval was 6.0 milligrams or

$$\frac{6 \times 10^{-3}}{12} = 5.0 \times 10^{-4} \text{ moles. This results in a reaction efficiency of}$$

$$\frac{5.0 \times 10^{-4}}{29.2 \times 10^{-4}} = 0.17 \text{ if the carbon monoxide reaction is assumed to be the primary reaction.}$$

This may be interpreted to mean that approximately one out of six oxygen atoms which enter the reaction system reacts with the graphite specimen. In the case of the 5 w/o vanadium additive, the most reactive tested, the efficiency was 0.61 or approximately one out of every two oxygen atoms reacting.

4. D Mechanical Properties Screening Studies

It was stated previously that tensile strength and flexural strength were selected as prime mechanical properties to be determined on the graphite base materials produced in this program. The reasons for this election of possible tests are many and will not be discussed here. Suffice to say that for the type of performance indication and mechanical design information desired, these two properties are perhaps paramount for brittle materials. For a screening study, they are sufficient to determine basic changes in performance as a function of compositional variables.

The tensile and flexural strength tests were performed in three different laboratories. This was done to obtain the maximum information from equipment of differing temperature capabilities, consistent with reasonable expenditures. It also furnished data on comparison of the same types of tests conducted in a variety of facilities. Room temperature tensile tests were carried out at the Astronuclear Laboratory, Westinghouse Research Center and the Southern Research Institute. Tensile and flexural strength tests at 2400°F were conducted at the Westinghouse Research Center. Tensile

and flexural strength tests at 4000°F were performed at the Southern Research Institute. Room temperature tests were run in the ambient atmosphere. Tests at 2400°F were run in a vacuum or at one atmosphere pressure of pure argon. Tests at 4000°F were made in one atmosphere pressure of pure argon.

The design of suitable tensile and flexural test specimens was based on a brittle material test philosophy. Since graphite-base materials exhibit essentially no ductility, even at the high temperatures used in some of this work, it was necessary to carefully design the specimens and grip assemblies to eliminate bi-axial or tri-axial stresses to the greatest extent possible. Only in true uniaxial loading is it possible to obtain an accurate value of the material strength, unaffected by stress components which might induce bending moments and cause premature fracture at low stress levels. Drawings of the specimens used for these tests in the different laboratories are shown in Figure 3.

The Southern Research Institute has found their tensile specimen design very satisfactory for many brittle materials, including graphite, over wide temperature ranges. The collet-type split grip inserts eliminate any specimen slippage in the grips during loading and also provide sufficient surface contact area to prevent localized fracture due to high stress concentration. The 1-inch gauge length has a slightly reduced cross-section at its center to promote fracture in this region, rather than at the extreme ends of the gauge length or outside the gauge length altogether. Numerous tests by Southern Research on different shapes of reduced section (varying radii of curvature) have resulted in selection of a geometry which does not introduce a measurable stress-concentration factor into this area, yet provides enough unit cross-sectional load increase to cause preferential fracture in the center of the gauge length.

Southern Research Institute has developed a unique tensile test facility which makes use of gas-bearings in the upper and lower sections of the load train. These bearings replace the conventional mechanical universal joints which are installed between the specimen grip assembly and the pull rods to eliminate bi-axial or tri-axial stresses on the specimen. A high pressure film of nitrogen gas supports the spherical bearings and provides an absolutely frictionless universal joint. The success of this system in providing true uniaxial

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SPECIMEN GEOMETRIES FOR MECH. PROP. TESTS

Figure 3

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loading has been demonstrated in numerous test programs on various brittle materials. One important result of this technique is to reduce the spread between values of tensile strength measured on specimens of the same material. It will be shown in the section on experimental results that the tensile test results reported by Southern Research Institute on the various materials tested in this program demonstrate more reproducible sets of values and higher average strength levels than the tests conducted on the same materials in the other two laboratories. Since the spread between tensile test results is greatly reduced by the use of a gas-bearing system, fewer specimens are needed to obtain a reliable average value on any given composition. A detailed description of the gas-bearing tensile test facility at Southern Research Institute is contained in a recent publication⁽⁵⁾.

The Westinghouse tensile specimen design was based on experimentation combined with application of available knowledge on the general mechanical behavior of graphite. It was decided to use a tapered specimen with no sharp angles to reduce any tendency toward stress-concentration failure. Therefore, a wedge type grip assembly was used to hold the ends of the specimen. The wedge tapered down gradually from both ends to the constant cross-section 1-1/2 inch gauge length. It was found that unless the wedge grip inserts were machined precisely the specimen would tend to slip downward in the grips as the load was increased, due to compression of material and forcing apart of the grip inserts. This could lead to inaccurate strain measurements as a function of applied load. By checking dimensions and fit of all inserts carefully, it was found possible to eliminate the slippage problem and produce satisfactory results. Since the center of the gauge length did not contain a reduced cross-section, breakage generally occurred at the end of the gauge length, at the point where the section thickness begins to increase. The stress values are still accurate, however, as long as breakage occurs within the specified gauge length cross-sectional area.

The design of flexural specimens did not present as difficult a problem due to the nature of the test itself. Since the test stock was 3/8" diameter rod, a miniaturized type of flexure test was conducted using much smaller specimens than conventionally

employed in this mechanical property test. Southern Research Institute used round rod specimens with a four-point loading system. The entire flexure test assembly was made of high strength graphite. Westinghouse used rectangular bar specimens milled from the round rod stock and employed a three point loading system. This assembly, too, was constructed of structural graphite. Direct resistance heating was used in the Westinghouse flexure tests. All other elevated temperature tests, flexure and tensile, in both laboratories were heated by radiant resistance or radiant induction methods.

Slow strain rates were used in the tensile and flexural strength tests. A nominal .005 in/in/min strain rate for both types of tests was considered to be reasonable for a brittle material such as graphite. Since no yield point was exhibited, this strain rate was maintained to fracture. Pertinent data were recorded during the running of the tests and is reported in detail in the next section dealing with the actual experimental results.

Specimen temperatures were measured by thermocouples for the 2400°F tests and by optical pyrometer for tests at 4000°F.

5. Experimental Results

As discussed previously, four categories of chemical composition were used to delineate the effects of additives and the effects of fuel on the properties of a reference matrix graphite composition. To review, these categories were:

- (1) Base matrix material - unfueled and undoped
- (2) Base matrix material containing additives
- (3) Base matrix material containing fuel (maximum loading)
- (4) Base matrix material containing both fuel and additives

In addition, two thermal treatments were used in processing to simulate the effects of normal and abnormal reactor operation:

- (1) Normal process cycle with final firing of material at 1900°C for six hours (Standard production procedure).
- (2) Final firing of material at 2750°C for 2 hours to provide a "sensitization" treatment simulating reactor heating to a temperature far above that expected during normal full power operation.

Two general types of testing on the classes of materials treated in this manner were used for screening purposes:

- (1) Oxidation tests at elevated temperature in a dynamic system using flowing air.
- (2) Mechanical property tests from room temperature to highest expected operating temperature (4000°F). Tensile tests and flexural strength tests were the two types of testing used, for reasons which have been described previously.

The purpose of this section of the report is to present the data obtained in order to determine the qualitative property trends resulting from the compositional and thermal treatment variations in the selected materials. It must be borne in mind that there were a large number of additives to be considered which made it impossible to investigate each in the detail which was desired, due to economic and time limitations in this phase of the overall program. The main objective was to perform enough qualitative type investigations to be in a position at the end of the screening program to select one or more additive compositions that exhibited superior performance in the chosen tests. In the second phase of the program the intention would be to more thoroughly investigate the selected few additives and thereby provide a reasonable amount of quantitative data for a more thorough evaluation. Therefore, it will appear that some of the data are incomplete and perhaps even marginal for making decisions on preferred materials. However, a closer study will reveal that there are significant differences between satisfactory and unsatisfactory materials which are obvious even with the limited amount of testing performed on any one composition. Primary emphasis was placed on the oxidation behavior, since a material for increased burnup application would not be deemed suitable if oxidation rates were enhanced, even if superior mechanical properties were realized. Similarly, a material that demonstrated extreme mechanical weakness under normal process treatment because of the presence of an additive would be considered reluctantly as a promising candidate, even though it might exhibit increased oxidation as compared to a standard reference material.

It will be noted in the following presentation of results that the largest quantity of work was performed on unfueled materials. There were two reasons for this. First, pyrocarbon coated fuel particles were not received until half the time available for the study had passed. This was due to difficulties associated with procuring natural or depleted

uranium bearing carbide particles to meet the purity requirements of production fuels. Second, the fuel particles were quite expensive, and the amount of testing had to be limited to stay within the economic bounds of the program. Consequently, the fuel-additive compositions for evaluation were chosen on the basis of results previously obtained on unfueled materials containing additives. Those compositions exhibiting the highest oxidation rates, combined with adequate maintenance of strength at elevated temperature, were selected.

The one exception was the ZrC additive, which was included as a low oxidation control for comparison purposes.

5. A. Oxidation Screening Studies

The purpose of the oxidation test screening program was to determine, by a simple reproducible test, the beneficial effect of additives in accelerating the oxidation rate of fueled and unfueled graphite-base materials. Toward this end, and as described previously, experimental conditions were designed to simulate re-entry of a small particle in the high velocity, high altitude transition-flow or free molecule flow regime. Since it is impossible at the present time to experimentally reproduce a complete trajectory, the selection of one arbitrary point along a trajectory curve was dictated by the necessity of achieving at least measurable oxidation mass losses on a small particle. But excessive oxidation was not desired since the particle would be consumed or the geometry changed so rapidly that an accurate differential rate could not be calculated. Thus, a rarefied, high altitude test point was indicated where mass flow rates of air would be low and easily handled in the laboratory apparatus. For this purpose, a temperature of 1200°C, a pressure of 0.1 Torr and a flow velocity of 1100 cm/sec were used.

The results of the oxidation studies are contained in Table V. There are two general ways of reporting oxidation rates, and they are both included here. The first is the conventional weight loss versus time value, in this case reported for the longest (20 minute) run. As discussed in a prior section, two runs (10 min and 20 min) were made for each additive material. All plotted rate data on additives which increased oxidation produced straight lines passing through the origin. Hence, two carefully measured data points were sufficient to define each curve.

Table V

Oxidation Tests on Unfueled and Fueled Materials

<u>Composition</u>	<u>Temp. ($^{\circ}$C)</u>	<u>% Wt. Loss (20 min run)</u>	<u>Oxidation Rate (atoms/cm²-min) $\times 10^{19}$</u>
Reference	1200 $^{\circ}$ C	11.8	2.77
Reference (sens.)	1200 $^{\circ}$ C	11.8	2.77
Reference	1000 $^{\circ}$ C	4.58	1.16
Reference	1400 $^{\circ}$ C	22.5	5.72
1 w/o WC	1200 $^{\circ}$ C	10.5	2.70
1 w/o WC (sens)	1200 $^{\circ}$ C	16.2	4.57
5 w/o WC	1200 $^{\circ}$ C	15.5	4.12
5 w/o WC (sens)	1200 $^{\circ}$ C	20.5	5.97
1 w/o Mo ₂ C	1200 $^{\circ}$ C	19.6	4.99
1 w/o Mo ₂ C (sens)	1200 $^{\circ}$ C	18.1	4.81
5 w/o Mo ₂ C	1200 $^{\circ}$ C	20.7	5.46
5 w/o Mo ₂ C (sens)	1200 $^{\circ}$ C	24.0	6.12
1 w/o ZrC	1200 $^{\circ}$ C	13.9	3.57
5 w/o ZrC	1200 $^{\circ}$ C	12.0	3.08
1 w/o NbC	1200 $^{\circ}$ C	9.5	2.78
1 w/o NbC (sens)	1200 $^{\circ}$ C	12.2	3.62
5 w/o NbC	1200 $^{\circ}$ C	16.0	4.53
5 w/o NbC (sens)	1200 $^{\circ}$ C	10.8	3.08

Table V (continued)

<u>Composition</u>	<u>Temp. (°C)</u>	<u>% Wt. Loss (20 min run)</u>	<u>Oxidation Rate (atoms/cm²-min) x 10¹⁹</u>
1 w/o TaC	1200°C	13.2	3.25
5 w/o TaC	1200°C	14.0	3.33
1 w/o Re	1200°C	17.8	4.40
1 w/o Ti	1200°C	13.0	3.57
5 w/o Ti	1200°C	12.0	3.40
1 w/o B ₄ C	1200°C	6.7	1.95
5 w/o B ₄ C	1200°C	6.9	1.76
1 w/o VC	1200°C	25.8	6.73
5 w/o VC	1200°C	26.1	6.84
1 w/o Ta ₂ N	1200°C	10.7	3.05
5 w/o Ta ₂ N	1200°C	12.7	3.52
1 w/o ZrN	1200°C	9.6	2.74
5 w/o ZrN	1200°C	16.3	4.30
1 w/o WB	1200°C	16.0	4.31
5 w/o WB	1200°C	19.9	5.21
1 w/o ZrB ₂	1200°C	12.6	3.28
5 w/o ZrB ₂	1200°C	7.0	2.04
1 w/o TiB ₂	1200°C	6.2	1.76
5 w/o TiB ₂	1200°C	6.3	1.84

Table V (continued)

<u>Composition</u>	<u>Temp. (°C)</u>	<u>% Wt. Loss (20 min run)</u>	<u>Oxidation Rate (atoms/cm²-min) x 10¹⁹</u>
1 w/o NbB ₂	1200°C	8.8	2.23
5 w/o NbB ₂	1200°C	7.9	2.21
1 w/o TaSi ₂	1200°C	11.4	2.75
5 w/o TaSi ₂	1200°C	12.7	3.08
1 w/o WSi ₂	1200°C	13.6	3.86
5 w/o WSi ₂	1200°C	17.7	4.47
Reference + UC ₂	1200°C	16.2	4.08
Reference + UC ₂ (sens)	1200°C	15.2	4.15
5 w/o WC + UC ₂	1200°C	31.3	8.51
5 w/o Mo ₂ C + UC ₂	1200°C	27.3	6.91
5 w/o Mo ₂ C + UC ₂ (sens)	1200°C	22.3	6.30
5 w/o VC + UC ₂	1200°C	25.3	6.94
5 w/o VC + UC ₂ (sens)	1200°C	15.8	4.21
1 w/o Re + UC ₂	1200°C	22.6	6.68
5 w/o Zr + UC ₂	1200°C	19.6	5.38

The first method of reporting oxidation merely defines the total percentage weight loss on a given specimen, and is not normalized to account for density differences between specimens of different compositions. This is of real importance in the case of the higher density fueled materials. Therefore, to determine the actual relationship of the available surface area to the oxidation rate, it is necessary to normalize the densities by a suitable factor, and to report the results in terms of reaction rate of surface carbon atoms per square centimeter per minute. When this is done, the second set of values is obtained. For comparison purposes, the latter results are more meaningful in determining rates of a surface-controlled process such as oxidation. Therefore, relative enhancement of oxidation by different additives is judged on the basis of these results rather than by total weight loss. Graphical interpretations of the oxidation rate data are contained in Figure 4-6.

Another factor beside density must be considered when comparing the oxidation rates of unfueled and fueled materials. This involves the relative proportion of oxidation among the graphite matrix, the additive and the fuel particles. On the reference unfueled material the dn/dt is accurately designated as the number of reacted carbon atoms per unit area per unit time, since there is no other component present in the system. In a reference material containing additives, some oxidation of the additive is occurring as well as well as oxidation of the matrix. The dn/dt is still assumed to represent carbon atom oxidation since no analyses of the additive reaction products have been made as part of this study. In the fueled materials containing additives, an additional oxidizing component is present in the form of the fuel particles. Again the oxidation rate (dn/dt) is assumed to represent carbon atom oxidation, although the three components in the system are oxidizing at different rates. During the next phase of the study chemical analyses will be made on selected compositions before and after oxidation tests to help determine the degree of reaction of each of the components.

In view of the above, it is best to compare oxidation test results on the basis of two categories of materials—fueled and unfueled. The effects of the additives in accelerating the oxidation of an unfueled reference material can then be determined on essentially an

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OXIDATION TESTS ON UNFUELED MATERIALS (1 w/o add.)

Figure 4

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OXIDATION TESTS ON UNFUELED MATERIALS (5 w/o add.)

Figure 5

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OXIDATION TESTS ON FUELED MATERIALS

Figure 6

equal density basis and will be directly related to the dn/dt value on an equal area basis. Likewise, for the fueled materials the effects on oxidation can be related to an essentially equal density and identical composition material by comparing additive-fuel combinations only with the fueled reference material. In this way, the contribution of fuel oxidation to the overall reaction rate can be neutralized and any increase over the reference level can be attributed to the additive itself.

Taking the additives by groups in the unfueled category, it may be seen that the metal carbides generally increase the oxidation rate of the base material more than the borides, nitrides, or silicides. The two exceptions are ZrC and B_4C . The former probably forms an oxidation inhibiting ZrO_2 complex which restricts the oxidation rate to only moderate increases over the undoped material. The latter, in common with all other boron-containing compounds (except WB), greatly retards the oxidation rate and in several cases reduces it below that of the reference material. The nitrides and silicides promote moderate increases in oxidation rate, but generally are not as satisfactory as the carbides. Rhenium metal is unique in being an elemental addition rather than a compound. Its high melting point, inertness to hydrogen and reluctance to form a stable carbide makes it an attractive candidate for a non-reactive additive in the reducing environment of the reactor. Rhenium forms an extremely low-melting point, low boiling point oxide and, as determined by experiment, greatly increases the oxidation rate of the graphite base material with an addition as low as 1 w/o Re.

There is a tendency for the 5 w/o additions of additive to increase the oxidation rate above that of the 1 w/o level. However, in some cases the increase is quite small and in other cases an apparent decrease in oxidation has occurred. Except for the WC , NbC , and ZrN additions there does not seem to be much to be gained by incorporation of quantities of material above the 1 w/o figure. There are no process problems involved in producing materials with 5 w/o additions. The main concern would be with the material economics and with the greater effects on core reactivity of the larger amount of additive present.

The sensitization treatment was intended to increase the oxidation rate of the materials tested. Such an effect was seen in the case of WC. There was little effect noted in the case of Mo_2C and NbC . The fueled materials showed decreases in oxidation when sensitized. Only a few of the additive materials were sensitized in the screening study. The purpose was merely to detect a trend, if one existed, which would result in further enhancement of oxidation. In the next phase of the program, more extensive sensitization treatments will be performed on the most promising additives to determine if sensitization is actually advantageous.

The addition of fuel particles to the reference matrix produced significant increases in the oxidation rate. This would be expected since UC_2 is another easily oxidizable additive. Its incorporation in a graphite matrix in large quantities would be expected to increase the oxidation rate. It was further demonstrated that the addition of WC, Mo_2C , VC, Re, and ZrC to a fueled graphite base increased the oxidation rate above that of the ordinary fueled material. Thus, the compositions containing both fuel and additives exhibited the highest oxidation rates of any of the groups tested.

The effects of temperature were investigated to a limited extent on the reference material. Tests conducted at 1000°C instead of the normal 1200°C resulted in an oxidation rate approximately half that at the higher temperature. Tests performed at 1400°C showed an accelerated oxidation rate, approximately double that at the 1200°C test point. In the follow-on program it is planned to do more extensive work on temperature effects for the most promising additives. On the basis of the oxidation tests conducted during the screening program, the additives WC, Mo_2C , VC, and Re were selected for more detailed study in the next phase of the project.

5.B Mechanical Properties Screening Studies

The purpose of the mechanical property studies was to ascertain in a semi-quantitative manner the effect of additives on the strength of fueled and unfueled materials as a function of temperature. The effects depend on the particular thermal process treatment used. For normal processing, culminating in a 6-hr. firing cycle at 1900°C , it is hoped that the additives would strengthen the material upon subsequent

testing for additive-bearing materials. This treatment, as explained previously, is designed to accelerate the primary destruct mechanism. Therefore, the interaction of additives with the matrix should contribute to a weakening of the high temperature strength of the fuel element material and thereby permit easier fragmentation of the reactor when it is destroyed.

Table VI lists the tensile test results obtained on all the unfueled materials containing additives, both in the normally processed and sensitized conditions. An attempt was made to cover as much territory as possible with the number of tests which could be made. Most materials had room temperature, 2400°F and 4000°F tests performed to determine the general shape of the temperature-strength curve. All tests were in the longitudinal (extrusion) direction. The small diameter of the rods precluded the testing of transverse samples.

In all cases but one, the tensile strength curves rise with an increase of temperature up to 4000°F, typical of graphite-base materials. The additives in the normal process material contribute to a general strengthening effect at all temperatures. Some additives are more effective than others, with 1 w/o Re and 1 w/o VC additions being particularly useful in raising the strength level both at room and elevated temperature. The carbides and rhenium exhibit the highest strengths at 4000°F. The sensitization treatment caused a significant reduction of strength as shown by subsequent tests at the same temperatures as the normal process material. The carbide additives as a group appear to confer a slightly greater overall strengthening than the boride, silicide, or nitride groups.

In order to obtain a better picture of the strengthening effects of additives on unfueled graphite, results are plotted in Figure 7 for the carbide additives and Re, and in Figure 8 for the nitrides, borides, and silicides. It is noted from these curves that the additives exert a significant effect in raising the fracture stress of the base material at all temperatures. The 1 w/o WB composition is the sole exception in the category of normally processed material. The great weakening effect of sensitization also may be seen in the cases of the 1 w/o Mo_2C and the 1 w/o NbC compositions, the only ones sensitized.

Table VI
Tensile Tests on Unfueled Materials

<u>Composition⁽¹⁾</u>	<u>Thermal Treatment</u>	<u>Test⁽²⁾ Laboratory</u>	<u>Test Temp. (°F)</u>	<u>Fracture⁽³⁾ Stress (psi)</u>
Reference	Normal	WANL	R. T.	3905
		WRL	R. T.	4025
		SRI	R. T.	5195
		WRL	2400	4580
		SRI	4000	8340
1 w/o WC	Normal	WANL	R. T.	4160
		WRL	2400	6850
		SRI	4000	8310
	Sensitized	WANL	R. T.	2795
		SRI	4000	7085
5 w/o WC	Normal	WANL	--	--
		WRL	2400	6250
		SRI	4000	8670
	Sensitized	WANL	R. T.	3505
		SRI	4000	7190
1 w/o Mo ₂ C	Normal	WANL	R. T.	4070
		WRL	2400	5850
		SRI	4000	8310
	Sensitized	WANL	R. T.	3140
		WANL	2400	4530
		SRI	4000	4500

(1) w/o refers to weight of metal constituent in graphite matrix.

(2) WANL - Astronuclear Laboratory

WRL - Research Center

SRI - Southern Research Institute

(3) Single tests - Actual value

Multiple tests - Average value

Table VI(continued)

<u>Composition</u>	<u>Thermal Treatment</u>	<u>Test Laboratory</u>	<u>Test Temp. (°F)</u>	<u>Fracture Stress (psi)</u>
5 w/o Mo ₂ C	Normal	WANL	R. T.	5250
		WRL	2400	6630
		SRI	4000	5100
	Sensitized	WANL	R. T.	4290
		WRL	2400	5360
		SRI	4000	6970
1 w/o NbC	Normal	WANL	R. T.	5750
		WRL	2400	6740
		SRI	4000	8260
	Sensitized	WANL	R. T.	3580
		WRL	2400	4560
		SRI	4000	6665
5 w/o NbC	Normal	WANL	R. T.	5190
		WRL	2400	7040
		SRI	4000	8510
1 w/o ZrC	Normal	WANL	R. T.	4570
		WRL	2400	3900
		SRI	4000	6630
5 w/o ZrC	Normal	WANL	R. T.	4720
		WRL	2400	6610
		SRI	4000	8505
1 w/o TiC	Normal	WANL	R. T.	5630
		WRL	2400	6280
5 w/o TiC	Normal	WANL	R. T.	5620
		WRL	2400	7110
1 w/o TaC	Normal	WANL	R. T.	4200
		WRL	2400	7460
5 w/o TaC	Normal	WANL	R. T.	4475
		WRL	2400	5220
		SRI	4000	8730

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Table VI (continued)

Composition	Thermal Treatment	Test Laboratory	Test Temp. (°F)	Fracture Stress (psi)
1 w/o Re	Normal	WANL	R. T.	5130
		WRL	2400	7080
		SRI	4000	9040
1 w/o B ₄ C	Normal	WANL	R. T.	4545
5 w/o B ₄ C	Normal	WANL	R. T.	3700
		SRI	4000	7065
1 w/o V	Normal	WANL	R. T.	5020
		WRL	2400	7160
		SRI	4000	9040
5 w/o V	Normal	WANL	R. T.	4155
		SRI	4000	5730
1 w/o WB	Normal	WANL	R. T.	3660
		WRL	2400	4020
5 w/o WB	Normal	WANL	R. T.	3420
		SRI	4000	7420
1 w/o ZrB ₂	Normal	WANL	R. T.	4200
5 w/o ZrB ₂	Normal	WANL	R. T.	3450
		WRL	2400	6940
1 w/o TiB ₂	Normal	WANL	R. T.	3330
5 w/o TiB ₂	Normal	WANL	R. T.	4330
		WRL	2400	5890
1 w/o NbB ₂	Normal	WANL	R. T.	3655
5 w/o NbB ₂	Normal	WANL	R. T.	3930
1 w/o Ta ₂ N	Normal	WANL	R. T.	5580
		WRL	2400	7110
5 w/o Ta ₂ N	Normal	WANL	R. T.	4430
		SRI	4000	7710
1 w/o ZrN	Normal	WANL	R. T.	3310
5 w/o ZrN	Normal	WANL	R. T.	4530
		WRL	2400	6340

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Table VI (continued)

<u>Composition</u>	<u>Thermal Treatment</u>	<u>Test Laboratory</u>	<u>Test Temp. (°F)</u>	<u>Fracture Stress (psi)</u>
1 w/o TaSi ₂	Normal	WANL	R. T.	4170
		WRL	2400	6840
5 w/o TaSi ₂	Normal	WANL	R. T.	3960
		SRI	4000	7040
1 w/o WSi ₂	Normal	WANL	R. T.	3900
5 w/o WSi ₂	Normal	WANL	R. T.	5680
		WRL	2400	7210

SELECTED TENSILE TEST RESULTS ON UNFUELED MATERIALS

Figure 7

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SELECTED TENSILE TEST RESULTS ON UNFUELED MATERIALS

Figure 8

Table VII lists the tensile test results obtained on the fueled materials containing additives. The reference fuel material exhibits a lower tensile strength than the unfueled reference material, particularly noticeable at the 4000°F temperature. The additives do not succeed in raising the strength of the fueled material to a marked extent, except for the 5 w/o Mo_2C additive which provided about a 15% increase in strength at 4000°F. None of the fueled additive materials at any test temperature approach the strength levels of the unfueled materials containing the same type and amount of additive. The additives WC, Mo_2C , VC, and Re were chosen for incorporation in the fueled material because they exhibited the best combination of enhanced oxidation and strength increase of those additives tested in the unfueled materials. The ZrC was incorporated in this series of fueled materials as a comparative additive. Its function was to illustrate the difference between the most promising additives and one of the average materials which did not appreciably increase both the strength and the oxidation rate of the unfueled reference material. Figure 9 is a plot of the tensile test results which illustrates the differences between the various additive-fuel specimens.

Table VIII contains the flexural strength test results on the unfueled materials containing additives. These test specimens were also prepared from longitudinal (extrusion) direction rod samples. The same general trend is seen for the strengthening effect as a function of the type and quantity of additive. Again, the carbides appear to be generally superior from the standpoint of conferring overall maximum strengthening effect up to the highest test temperature. Figure 10 is a plot of the data for those additives on which two test temperatures were used. It would have been desirable to have more test points on these carbides, as well as multiple points for the other additives, but it was not feasible to accomplish this in the screening program. It is planned to obtain more detailed data of this nature on the most promising additives in the next phase of the study. From the limited data available, it appears that sensitization reduced the flexural strength considerably, similar to the effects of sensitization on tensile properties.

Table IX lists the results of flexural strength tests on fueled materials containing additives. It is seen that the fueled reference material exhibits lower strength at room and elevated temperatures than the unfueled reference material. The additives used (WC, Mo_2C , VC, ZrC, and Re) are not effective in raising the flexural strength

Table VII

Tensile Tests on Fueled Materials

<u>Composition</u>	<u>Thermal Treatment</u>	<u>Test Laboratory</u>	<u>Test Temp. (°F)</u>	<u>Fracture Stress (psi)</u>	
Reference + UC ₂	Normal	WANL	R. T.	3185	
		WRL	2400	5160	
		SRI	4000	6670	
5 Mo ₂ C + UC ₂	Sensitized	SRI	4000	5265	
	Normal	WANL	R. T.	4035	
		WRL	2400	5670	
		SRI	4000	7670	
	Sensitized	SRI	4000	5480	
	5 WC + UC ₂	Normal	WANL	R. T.	3640
WRL			2400	4730	
SRI			4000	6370	
5VC + UC ₂	Normal	WANL	R. T.	3210	
		WRL	2400	4590	
		SRI	4000	6070	
	Sensitized	SRI	4000	4450	
	1 Re + UC ₂	Normal	WANL	R. T.	3675
			WRL	2400	5560
SRI			4000	7240	
5 Zr + UC ₂	Normal	WANL	R. T.	3075	
		WRL	2400	4380	
		SRI	4000	6690

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SELECTED TENSILE STRENGTH TEST RESULTS ON FUELED MATERIALS

Figure 9

Table VIII
Flexural Strength Tests on Unfueled Materials

<u>Composition</u>	<u>Thermal Treatment</u>	<u>Test Laboratory</u>	<u>Test Temp. (°F)</u>	<u>Fracture Stress (psi)</u>
Reference	Normal	WRL	R.T.	6330
		SRI	R.T.	6760
		WRL	2400	8910
		SRI	4000	11135
1 w/o WC	Normal	WRL	R.T.	6640
		WRL	2400	8970
5 w/o WC	Normal	WRL	R.T.	7620
		SRI	4000	13190
1 w/o Mo ₂ C	Normal	WRL	R.T.	7230
		WRL	2400	8440
5 w/o Mo ₂ C	Normal	WRL	R.T.	7190
		SRI	4000	10980
1 w/o NbC	Normal	WRL	R.T.	4090
		WRL	2400	8150
	Sensitized	WRL	R.T.	4440
		WRL	2400	5580
5 w/o NbC	Normal	WRL	R.T.	6490
		SRI	4000	11840
1 w/o ZrC	Normal	WRL	R.T.	6570
		WRL	2400	8700
5 w/o ZrC	Normal	SRI	4000	10750
5 w/o TiC	Normal	WRL	2400	9000
1 w/o TaC	Normal	WRL	2400	9930
5 w/o TaC	Normal	SRI	4000	12400
1 w/o Re	Normal	WRL	2400	10180
1 w/o B ₄ C	Normal	WRL	2400	8760
5 w/o B ₄ C	Normal	WRL	2400	7160

Table VIII (continued)

<u>Composition</u>	<u>Thermal Treatment</u>	<u>Test Laboratory</u>	<u>Test Temp. (°F)</u>	<u>Fracture Stress (psi)</u>
1 w/o VC	Normal	WRL	2400	7830
5 w/o VC	Normal	SRI	4000	6865
1 w/o WB	Normal	WRL	2400	7900
5 w/o WB	Normal	SRI	4000	12100
1 w/o ZrB ₂	Normal	WRL	2400	8310
5 w/o ZrB ₂	Normal	WRL	2400	8240
1 w/o TiB ₂	Normal	WRL	2400	8070
5 w/o TiB ₂	Normal	WRL	2400	8210
1 w/o NbB ₂	Normal	WRL	2400	7620
5 w/o NbB ₂	Normal	WRL	2400	7240
1 w/o Ta ₂ N	Normal	WRL	2400	8860
5 w/o Ta ₂ N	Normal	SRI	4000	10550
1 w/o ZrN	Normal	WRL	2400	8750
5 w/o ZrN	Normal	WRL	2400	8370
1 w/o TaSi ₂	Normal	WRL	2400	8760
5 w/o TaSi ₂	Normal	SRI	4000	7910
1 w/o WSi ₂	Normal	WRL	2400	8650
5 w/o WSi ₂	Normal	WRL	2400	9300

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SELECTED FLEXURAL STRENGTH TEST RESULTS ON UNFUELED MATERIALS

Figure 10

Table IX

Flexural Strength Tests on Fueled Materials

<u>Composition</u>	<u>Thermal Treatment</u>	<u>Test Laboratory</u>	<u>Test Temp. (°F)</u>	<u>Fracture Stress (psi)</u>
Reference + UC ₂	Normal	SRI	R. T.	5770
		WRL	2400	6560
		SRI	4000	8810
	Sensitized	SRI	R. T.	4190
		SRI	4000	5720
5 Mo ₂ C + UC ₂	Normal	SRI	R. T.	6015
		WRL	2400	8050
		SRI	4000	8390
	Sensitized	SRI	R. T.	6335
		SRI	4000	6615
5 WC + UC ₂	Normal	WRL	2400	7270
		SRI	4000	8440
5VC + UC ₂	Normal	SRI	R. T.	5205
		WRL	2400	5850
		SRI	4000	7720
	Sensitized	SRI	R. T.	4525
		SRI	4000	4990
1 Re + UC ₂	Normal	WRL	2400	7280
		SRI	400	8255
5 ZrC + UC ₂	Normal	WRL	2400	6670

level of the fueled material. In fact, the additives Mo_2C , WC, VC, and Re appear to lower the strength below that of the fueled reference material. Sensitization further decreases the strength of the fueled additive-bearing materials. Figure 11 illustrates the data for those fueled flexure specimens which were exposed to at least two temperatures.

The effects on strength of the best additives, therefore, are different in the fueled and unfueled materials. Whereas the additives WC, Mo_2C , VC, and Re effectively raise the tensile and flexural strength level of unfueled core material, they either tend to lower the strength of fueled core material or do not increase it measurably. These effects are noticeable at the three test temperatures investigated. This is a surprising result, and cannot be explained at the present time. Apparently the fuel particles exert a degrading influence on the matrix strengthening properties of the additives.

5. C Metallography

A limited amount of metallographic analysis was performed to determine the structure of matrix material after various thermal treatments, to discover how the additive material was dispersed in the matrix graphite, and to ascertain what effect the sensitization treatment might have on the distribution and appearance of the additive particles.

The results of these examinations are shown in the series of photomicrographs contained in Figures 12-16. The magnification is 250X in all cases. The resolution is not particularly good since the Polaroid technique was used, but sufficient detail is visible to observe the effects of the treatments.

Figure 12 illustrates the undoped material in the cured and baked states. Figure 13 shows the same material in the fired and "sensitized" conditions. The basic structure has not been altered by either of these treatments. However, the appearance of voids in the binder network may be noticed after the baking treatment and is further accentuated after the firing step. This is due to removal of volatile constituents in the binder as a result of progressively higher treatment temperatures. The irregular light gray shapes are the primary graphite flour particles. The darker gray, rather continuous phase, is a mixture of the binder and carbon black mixture. The binder constituent exhibits more porosity because of the coking effect of the thermal treatment. The larger black spots are voids in the structure, typical of materials of considerably less than theoretical density.

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SELECTED FLEXURAL TEST RESULTS ON FUELED MATERIALS

Figure 11

UNDOPED GRAPHITE CORE MATERIAL (CURED AT 250° C)
250 X

UNDOPED GRAPHITE CORE MATERIAL (BAKED AT 850° C)
250 X

UNDOPED GRAPHITE CORE MATERIAL (CURED AND BAKED)

Figure 12

UNDOPED GRAPHITE CORE MATERIAL (FIRED AT 1900° C)
250 X

UNDOPED GRAPHITE CORE MATERIAL (SENSITIZED AT 2750° C)
250 X

UNDOPED GRAPHITE CORE MATERIAL (FIRED AND SENSITIZED)

Figure 13

Figure 14 shows photos of the graphite reference material containing 5 w/o WC additive. The first picture was taken after the normal 1900°C firing treatment and shows the distribution of micron-size tungsten carbide particles in voids and grain boundaries. The second shot was taken after a 2750°C sensitization treatment. It appears that the particles have become much finer and more intimately distributed in the matrix as a result of this treatment.

Figure 15 shows the effects of firing and sensitization treatments on reference material containing 5 w/o Mo₂C additive. The initial and final additive particles sizes and the distribution appear to be approximately the same as for the material containing tungsten carbide.

Figure 16 includes photos of a reference material containing pyrocarbon coated UC₂ particles. The light circular particles are UC₂, surrounded by an irregular gray enclosure of pyrolytic carbon. The UC₂ particle diameter is approximately 100-microns, with coating thicknesses of about 25-microns. Of particular note is the fact that the coating is not in close contact with the surface of the UC₂ particle. This behavior is probably due to the different thermal expansion characteristics of the two materials, which results in separation of surfaces when the high temperature deposition is completed and the material cools to room temperature. There is no difference in the structure of the fueled material after the 1900°C firing cycle, as compared to that of the material after baking at 850°C. There is also no evidence of fuel "migration" through the pyrocarbon coating after 1900°C - 6 hour firing cycle.

6. Fundamental Studies of Oxidation

6.A Introduction

A separate study was funded under this project at the Westinghouse Research Center, the purpose of which was to determine some of the more fundamental aspects of the graphite oxidation process, particularly in high velocity gas streams. This study was conducted by Dr. E. A. Gulbransen in equipment especially constructed for this type of investigation. The general nature of the work was similar

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5 W/O WC IN GRAPHITE CORE MATERIAL (FIRED AT 1900° C)
250 X

5 W/O WC IN GRAPHITE CORE MATERIAL (SENSITIZED AT 2750° C)
250 X

5 w/o WC IN GRAPHITE CORE MATERIAL (FIRED AND SENSITIZED)

Figure 14

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5 w/o Mo_2C IN GRAPHITE CORE MATERIAL (FIRED AT 1900°C)
250 X

5 w/o Mo_2C IN GRAPHITE CORE MATERIAL (SENSITIZED AT 2750°C)
250 X

5 w/o Mo_2C IN GRAPHITE CORE MATERIAL (FIRED AND SENSITIZED)

Figure 15

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FUELED GRAPHITE CORE MATERIAL (BAKED AT 850° C)
250 X

FUELED GRAPHITE CORE MATERIAL (FIRED AT 1900° C)
250 X

FUELED GRAPHITE CORE MATERIAL (BAKED AND FIRED)

Figure 16

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to the concurrent oxidation study performed by G. Rymer of the Astronuclear Laboratory, but the pressure and flow velocities in Gulbransen's system were quite different. The results of the two studies are compared at the conclusion of this section. Some areas of difference in oxidation rates of additive materials were discovered and reasons are advanced to account for possible behavior leading to such differences. The work of Gulbransen provides a definitive study of the oxidation of pure graphite, with secondary emphasis on the oxidation characteristics of fuel matrix materials and additive compositions. Therefore, it provides a companion study to the work of Rymer, which was more concerned with the qualitative screening of additive-bearing materials.

The mechanism and kinetics of oxidation of graphite in air have been studied by numerous investigators. Early work was primarily confined to closed static system, whereas many of the more recent investigations have involved the use of dynamic (flow) conditions to determine the effects of high velocity air moving past the reacting surface. Walker, Rusinko, and Austin⁽⁶⁾ in 1959 made an extensive review of the kinetic data and mechanisms proposed for the oxidation reaction. Frank-Kamenetski⁽⁷⁾ reviewed the early Russian literature in 1947. Both reviews emphasize the shift in reaction mechanism from surface chemical reaction rate control to boundary layer diffusion control at high temperatures. Levy⁽⁸⁾ recently studied the combustion of graphite in air in a static system and showed the reaction was under chemical control below 843°C. Ragone and Zumwalt⁽⁹⁾ studied graphite corrosion in oxygen and determined that the corrosion rate reached a maximum at 1100° - 1200°C. Adsorption control kinetics were found to apply in this case. Gulbransen et. al.⁽¹⁰⁾ studied the oxidation of graphite from 600° - 1500°C at pressures of 2-76 Torr in a static reaction system. Below 700°C the oxidation was limited by an adsorption process, while above 700°C the rate was limited by gaseous diffusion of oxygen. In a more recent paper, Gulbransen et. al.⁽¹¹⁾ have studied the combustion of spectroscopic graphite in oxygen and air from 1000°C - 1400°C in a flow system. They concluded that the mobile adsorption of oxygen molecules is the rate-limiting process and that extremely rapid reaction rates apparently can be accounted for by this theory. It is postulated that pore diffusion is not rate-limiting. The nearly linear pressure dependence also supports the mobile adsorption mechanism for reaction.

Experimental and theoretical re-entry studies have also been made to determine the oxidation rate of fueled and unfueled graphite base materials in small particle sizes. Feild⁽²⁾ performed a digital computer study on burnup of small graphite spheres assumed to re-enter in a continuum flow regime according to the theory of S. M. Scala.⁽¹²⁾ He also conducted experimental investigations in an arc plasma wind tunnel designed to simulate the conditions of hypersonic flight along a re-entry trajectory.⁽²⁾ Experiment and theory were in fairly close agreement for the conditions studied. A more refined study by Bridges⁽³⁾ further delineated the environmental conditions associated with re-entry burnup of graphite particles. A recent theoretical analysis of the free molecule flow regime at high altitudes by Hargrove has succeeded in differentiating the characteristic behavior of graphite particles during re-entry in this regime as compared to that in the lower altitude continuum flow regime.⁽⁴⁾

It has been found in recent experimental work that the addition of small quantities of certain metal carbides in the form of fine powders to a graphite matrix significantly accelerated the oxidation rate over that of the undoped material. Two of the most promising additives studied were tungsten carbide and molybdenum carbide. The results of some additional work on graphite containing these two additives and exposed in a high temperature gas flow system are reported below. Both pure oxygen and pure air were used as the reactant gas. Oxidation rate data were obtained and compared to that of spectroscopic graphite and a reference base mixture under identical conditions.

6.B Experimental Procedure

6.B.1 Apparatus and Materials

Figure 17 shows a schematic drawing of the apparatus. The graphite specimen is suspended from one end of a Cahn Electrobalance enclosed in the reaction system (13). Oxygen or air is preheated and passed over the specimen. An auxiliary forepump or liquid helium trap is used to pump the gas through the system. The flow rate and gas pressure are maintained constant by a sensitive leak valve. The volume of gas used and the flow rate were calculated from measurements of the pressure change of a calibrated

gas reservoir. The system pressure and flow rate were changed by controlling the exit pumping speed and the volume of gas added through the leak valve.

Mass spectrometric analyses were made of part or all the gases used in the reaction. A liquid helium trap was used to condense all the gases.

The balance had a capacity of approximately 1-gram, a sensitivity of 10^{-5} g. for a 1-gram sample and a period of less than 0.1 second. A section of 8-mil platinum wire was used in the hot zone to support the sample. A section of 2-mil nickel-chromium wire was used in the cold zone.

A vacuum-tight high purity alumina furnace tube was used to enclose the sample, as shown in Figure 17. This tube was attached to the stainless steel connecting tubing by a stainless steel flange and a rubber "O" ring.

The furnace tube, balance housing and associated apparatus were attached to a series of mercury pumps and a fore pump. A liquid nitrogen or dry ice trap was used to condense mercury vapor. At 1200°C a vacuum of better than 10^{-5} Torr could be achieved readily.

A Kanthal-Super furnace was used, the construction and operation of which has been described.⁽¹⁴⁾ The specimen temperature was determined by a Pt-Pt + 10% Rh thermocouple mounted adjacent to the specimen inside the furnace tube. The thermocouple was calibrated to 1200°C . Maximum temperature variation of the furnace was $\pm 5^{\circ}\text{C}$.

Pure graphite specimens were machined from rods of spectroscopic purity graphite (AGKSP) obtained from the National Carbon Company. Nuclear reactor core graphite (reference material) was fabricated by extrusion, curing, baking, and firing selected graphite powders blended with the liquid carbonaceous binder. Mo_2C and WC procured from Firth-Sterling, Inc. (3 micron powders of 98 + % purity) were added in amounts of 1% and 5% by weight of contained metal. The standard specimen was a cylinder 0.050-grams in weight having a diameter of 0.32 cm, a length of 0.39 cm, and a surface area of 0.55 cm^2 . Commercial grade oxygen and air were used and the gases were dried before admission to the system.

REACTION SYSTEM

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Figure 17

6.B.2 Method

Specimens were placed on the balance, the system closed and then evacuated to a pressure of 10^{-5} Torr. The furnace was raised about the furnace tube and the vacuum read on an ion gauge or McLeod gauge. When the desired reaction temperature was reached, the auxiliary pump or helium trap was connected to the system for exhausting the gases. Oxygen or air was added directly from the reservoir to avoid contact of air with the mercury. The dry ice or liquid nitrogen trap was placed between the reaction system and mercury pumps to minimize mercury contamination.

Weight changes of the graphite specimen and pressure changes of the oxygen reservoir were read and recorded as a function of time. Oxygen or air pressure in the reaction system was maintained constant to ± 0.2 Torr. Readings were made at 15-second intervals. Continuous adjustment of the pressure was necessary to maintain constant pressure and reproducible balance readings.

To test for specimen spalling (fragmentation of graphite particles) the reaction was stopped at midpoint by quickly removing the gases and lowering the furnace. When spalling occurred, small graphite particles were found in the furnace tube. These particles were collected and weighed to determine the relative importance of this effect in contributing to mass loss.

6.C Experimental Results

6.C.1 Graphite Core Material

The oxidation behavior of spectroscopic graphite at 1200°C as a function of pressure and flow rate has been determined previously by Gulbransen et. al. ⁽⁶⁾

In this study it was found that the reaction rate was chemically controlled for this temperature in a flow system using small dimension specimens. Flow rates ranged from 7.6×10^{18} to 3.6×10^{20} atoms/second at pressures of 2-19 Torr. It was also found that the rate of combustion was essentially a zero order reaction for the flow rates and pressures used, depending only on time of exposure and not on concentration of the reactant species. This produced a straight line plot of weight loss versus time. The rates of oxidation were related to values extrapolated from earlier low temperature studies and to theoretical rates based on kinetic theory. Good agreement was found when correlation was made with

extrapolation of low temperature kinetic data using the experimentally determined heat of activation of 39,000 cal/mole. The experimental oxidation rates were up to 2.7% of theoretical, assuming all collisions resulted in reaction. Over 20% of the oxygen atoms passing through the system reacted with the graphite. Gas analyses of the reaction products suggested that carbon monoxide was the primary reaction product. A mechanism based on mobile adsorption of oxygen was confirmed.

Figure 18 compares the reaction rate in oxygen of the basic graphite reference material with that of spectroscopic graphite at an initial specimen temperature of 1200°C, a system pressure of 9.5 Torr absolute and an oxygen flow rate of 9.1×10^{19} atoms of oxygen per second. It is noted that the oxidation rate for the core material is considerably less than that of the pure graphite at exposure times up to 3 1/2-minutes duration. The difference in rates for specimens of the same geometry, and different materials may be caused by variations in the density, actual surface area, chemical purity of the surface, and activated surface sites of the two compositions.

The determination of oxidation characteristics of the basic graphite core material was made by measurement of the parameters shown in Table X. In this table, the system pressure was measured with a mercury manometer and the flow rate of atoms of gas per second in the system was calculated from the decrease in the calibrated gas reservoir pressure as a function of time. The controlled leak valve was adjusted so the reservoir pressure decreased linearly with time to provide a constant flow rate of gas. The estimated temperature is the calculated contribution of the exothermic heat of combustion of the carbon atoms to the initial specimen temperature. This temperature can be calculated assuming (1) CO is the primary reaction product, (2) the emissivity is unity, and (3) most of the heat loss is due to radiation. Faster oxidation rates produce higher estimated surface temperatures because of the greater amount of heat generated by the reaction. These temperatures were calculated from use of thermochemical values for heat of combustion of graphite as a function of temperature. Weight changes of the specimen as a function of time were obtained from the recording electrobalance. The rate dw/dt

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COMPARISON RATES OF OXIDATION IN OXYGEN

Figure 18

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Table X
Oxidation Rate versus Pressure and Flow
Reference Graphite-1200°C in Oxygen

Reaction Conditions					Rate of Oxidation		
Press Torr	Flow Atoms/sec	Estimated Temp. (°C)	$1/T \times 10^3$	$\frac{dw}{dt}$, g/sec	$\frac{dn}{dt}$ Atoms C/sec	$\frac{dn}{dt}$ $\frac{\text{atoms C}}{\text{cm}^2\text{-sec}}$	Log dn/dt
5	2.13×10^{19}	1214	.6724	5.86×10^{-5}	2.94×10^{18}	5.34×10^{18}	18.73
5	4.79×10^{19}	1230	.6653	1.24×10^{-4}	6.22×10^{18}	1.13×10^{19}	19.05
9.5	9.0×10^{19}	1261	.6518	2.65×10^{-4}	1.33×10^{19}	2.42×10^{19}	19.38
9.5	9.1×10^{19}	1251	.6561	2.20×10^{-4}	1.10×10^{19}	2.00×10^{19}	19.30
9.5	1.12×10^{20}	1270	.6480	3.09×10^{-4}	1.55×10^{19}	2.82×10^{19}	19.45
9.5	1.23×10^{20}	1280	.6439	3.55×10^{-4}	1.78×10^{19}	3.32×10^{19}	19.52
9.5	1.40×10^{20}	1278	.6447	3.42×10^{-4}	1.72×10^{19}	3.13×10^{19}	19.50
9.5	1.56×10^{20}	1280	.6439	3.51×10^{-4}	1.76×10^{19}	3.20×10^{19}	19.51

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in grams/sec was determined at time $t = 0$ before surface area changes occurred. The differential form of Lagrange's interpolation formula ⁽¹²⁾ was used to estimate the rate. Avogadro's number was used to convert the oxidation rate (dw/dt) to atoms of carbon per second (dn/dt). The total number of carbon atoms reacting per cm^2 per second was calculated from a knowledge of the original geometric surface area. The functions $1/T \times 10^3$ and $\log (dn/dt)$ were used to calculate the activation energy of the combustion reaction by means of an Arrhenius exponential plot.

The data in Table X indicate that the oxidation rate at 1200°C is dependent on the flow rate of gas past the surface and the pressure within the system. The latter conclusion is drawn from a comparison of the rate curves in Figures 20-21 where rates for the two pressures are plotted.

The reaction of the basic reference material with dry air at 1200°C was determined by a series of experiments conducted in the same manner as those employing oxygen. The same pressures and approximately the same flow rates were used. The results are shown in Table XI. It is seen from these data that the oxidation rates are considerably slower than with pure oxygen because of the dilution of the gas by nitrogen, which does not react with graphite at this temperature. Since the nitrogen comprises 80% of the available atoms in the flow, it would be expected that the reaction rate with the oxygen in air would be near 20% of the rates found in pure oxygen under the same flow conditions. Actually, the rates average about 18% of these in oxygen at the flow rates studied. The comparison of the oxidation rates in oxygen and air for the core material is depicted graphically in Figure 19. The reaction rates are dependent on the pressure at the two pressures studied, and are linearly dependent on the gas flow rate. The non-linearity of the reaction rate at higher flow rates of oxygen at 1200°C and 9.5 Torr pressure cannot be explained at present, but perhaps it may be due to the change of the reaction mechanism from that of complete chemical reaction rate control to partial diffusion rate control.

To disclose the effects of temperature on the mechanism and rate of the oxidation reaction of the core material at 1200°C and 5 Torr pressure, in oxygen and air, an Arrhenius plot was constructed. From this plot it was also possible to determine the activation energy required to initiate the reaction from a measurement of the slope of

Table XI

Oxidation Rate versus Pressure and Flow

Reference Graphite - 1200°C In Air

Reaction Conditions				Rate of Oxidation			
Press Torr	Flow Atoms/sec	Estimated Temp.		$\frac{dw}{dt}$, g/sec	$\frac{dn}{dt}$ Atoms C/sec	$\frac{dn}{dt}$ $\frac{\text{Atoms C}}{\text{cm}^2\text{-sec}}$	Log $\frac{dn}{dt}$
		(°C)	$\frac{1}{T} \times 10^3$				
5	1.76×10^{19}	1202	.6779	7.5×10^{-6}	3.77×10^{17}	6.85×10^{17}	17.84
5	5.00×10^{19}	1207	.6756	3.07×10^{-5}	1.54×10^{18}	2.80×10^{18}	18.45
9.5	8.90×10^{18}	1217	.6711	6.89×10^{-6}	3.46×10^{18}	6.29×10^{18}	18.80
9.5	1.14×10^{20}	1215	.6720	6.0×10^{-5}	3.01×10^{18}	5.47×10^{18}	18.74
9.5	1.33×10^{20}	1215	.6720	6.0×10^{-5}	3.01×10^{18}	5.47×10^{18}	18.74
9.5	1.31×10^{20}	1229	.6657	1.2×10^{-4}	6.03×10^{18}	1.10×10^{19}	19.04

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RATE OF OXIDATION VERSUS FLOW

Figure 19

the curve, thus furnishing means of comparing any theoretical mechanism energy requirement with the experimentally determined value. Figure 20 contains the standard Arrhenius plot of $\log dn/dt$ versus $1/T$ on measured and extrapolated data for the core material over a wide temperature range. In addition, there are interesting data comparing kinetic theory rate predictions with experimental values, and also direct calculations of the rate of surface recession of the material as a function of the oxidation rate. The line AB represents low temperature ($350^{\circ} - 700^{\circ}\text{C}$) oxidation rates in pure oxygen. The extrapolation to higher temperatures ($700^{\circ}\text{C} - 1500^{\circ}\text{C}$) is shown by line BC. It is seen that experimental values obtained at 1200°C fall on the extrapolated curve. Therefore, extrapolation of reaction rates to higher temperatures appears to be valid in the cases studied since there is no deviation from the straight line (exponential) function. It is also apparent that the reaction is chemically rate controlled throughout the temperature range studied. As shown by the surface recession rate on the right side of the plot, the oxidation rates are quite rapid at high temperatures and can lead to complete consumption of small graphite shapes in rather short time periods.

Calculations were made to determine the theoretical maximum reaction rates possible as a function of temperature, based on the kinetic theory of gases.⁽¹⁵⁾ Curves F and G illustrate these maxima. At 1200°C the actual rates are approximately 2 to 3 orders of magnitude lower than the theoretical. However, it is interesting to speculate on the shape of the extrapolated experimental curve at temperatures in the range of $2000^{\circ} - 2400^{\circ}\text{C}$, and wonder how close the theoretical rate curves may be approached. Future work is being planned to investigate this region in experimental apparatus suitably designed to operate in this temperature range.

A similar plot of data for the same core material at 1200°C and 9.5 Torr pressure is shown in Figure 21. The flow rates are normalized to permit comparison with Figure 20 on the basis of pressure as the only variable. There is some effect of pressure on the experimentally determined oxidation rates at 1200°C , with the higher pressure producing a somewhat higher rate.

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LOG dn/dt VERSUS $1/T$ (OXIDATION UNFUELED REFERENCE MATERIAL) 5 TORR

Figure 20

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LOG $\frac{dn}{dt}$ VERSUS 1/T (OXIDATION UNFUELED REFERENCE MATERIAL) 9.5 TORR

Figure 21

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The slopes of the curves in Figure 20 and 21, all of which are essentially the same, were based originally on an activation energy of 39,000 calories/mole, determined from earlier studies at lower temperatures.⁽¹⁶⁾ Since the valid extrapolation of these curves based on experimental evidence extends the exponential function, the same activation energy will apply at the higher temperature of this study. This value for ΔH is reasonable for a chemical reaction rate control mechanism, and is compatible with the "mobile adsorption of oxygen" mechanism proposed by Gulbransen.⁽¹¹⁾

6. C. 2 Graphite Core Material Containing Additives

Studies were conducted on specimens of nuclear core graphite containing intentional additions of powdered dispersions of tungsten carbide (WC) and molybdenum carbide (Mo_2C). Additions were 1% and 5% by weight of contained metal in the final mixture. The carbide particles were approximately 3 microns in diameter. Fabrication and processing of the material were carried out as described earlier in this report. The specimens were exposed to dry air in the oxidation apparatus under the same flow rates and pressures at 1200°C as were used previously for the undoped core material and the spectroscopic graphite.

The results of this investigation are tabulated in Table XII for the two additives and the two levels of doping. The plot of dn/dt versus air flow rate in Figure 22 indicates linear dependence of oxidation rate on this flow. The additives have no effect on the basic reaction mechanism at 1200°C under the flow and pressure conditions studied. There is, however, a measurable effect on the reaction rate as a function of the type and amount of the additive present. The 1 w/o tungsten addition causes an acceleration of the base oxidation rate at all flow levels as shown by Curve A in Figure 22. At a flow rate of 1.5×10^{20} atoms per second, the rate is approximately 40% higher than for the undoped material, shown by Curve E. The 5 w/o tungsten addition causes a slight retardation of oxidation rate (Curve B) below that of the undoped material. This is unexpected in view of the acceleration of the oxidation from the 1 w/o tungsten addition. It possibly could be due to oxidation inhibiting buildup of tungsten oxide on the surface which is not readily removed at the gas flow velocities used in the apparatus. In the case of the molybdenum additions, both the

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Table XII

Oxidation Rate versus Pressure, Flow and Additive
Reference Graphite - 1200°C In Air

Reaction Conditions				Rate of Oxidation			
Press Torr	Flow Atoms/sec	Estimated Temp. (°C)	$1/T \times 10^3$	$dw/dt, g/sec$	$dn/dt, atoms$ C/sec	dn/dt atoms C/cm ² -sec	Log dn/dt
Basic Mix + 1 w/o W							
5	8.1×10^{19}	1214	.6724	5.73×10^{-5}	2.88×10^{18}	5.24×10^{18}	18.72
9.5	6.6×10^{19}	1215	.6720	1.16×10^{-4}	3.21×10^{18}	5.84×10^{18}	18.77
9.5	1.2×10^{20}	1230	.6653	2.26×10^{-4}	6.26×10^{18}	1.14×10^{19}	19.06
9.5	1.3×10^{20}	1227	.6666	1.07×10^{-4}	5.38×10^{18}	$.98 \times 10^{19}$	18.99
9.5	1.54×10^{20}	1232	.6644	1.33×10^{-4}	6.68×10^{18}	1.21×10^{19}	19.08
9.5	2.4×10^{20}	1254	.6548	4.21×10^{-4}	1.17×10^{19}	2.13×10^{19}	19.33
Basic Mix + 5 w/o W							
5	6.06×10^{19}	1207	.6756	2.76×10^{-5}	1.38×10^{18}	2.51×10^{18}	18.40
9.5	9.1×10^{19}	1212	.6734	4.8×10^{-5}	2.41×10^{18}	4.38×10^{18}	18.64
9.5	1.38×10^{20}	1222	.6688	9.3×10^{-5}	4.7×10^{18}	8.54×10^{18}	18.93
9.5	1.46×10^{20}	1222	.6688	9.3×10^{-5}	4.7×10^{18}	8.54×10^{18}	18.93
Basic Mix + 1 w/o Mo							
5	5.74×10^{19}	1207	.6756	2.54×10^{-5}	1.27×10^{18}	2.31×10^{18}	18.36
9.5	9.2×10^{19}	1212	.6734	4.77×10^{-5}	2.39×10^{18}	4.35×10^{18}	18.64
9.5	1.28×10^{20}	1220	.6697	8.10×10^{-5}	4.07×10^{18}	7.40×10^{18}	18.87
Basic Mix + 5 w/o Mo							
5	5.37×10^{19}	1207	.6756	2.67×10^{-5}	1.36×10^{18}	2.47×10^{18}	18.39
9.5	9.4×10^{19}	1213	.6729	5.15×10^{-5}	2.58×10^{18}	4.69×10^{18}	18.67
9.5	1.0×10^{20}	1213	.6729	5.16×10^{-5}	2.59×10^{18}	4.71×10^{18}	18.67
9.5	1.28×10^{20}	1217	.6711	7.27×10^{-5}	3.65×10^{18}	6.64×10^{18}	18.82

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RATE OF OXIDATION VERSUS FLOW

Figure 22

1 w/o and 5 w/o levels decrease the oxidation rate somewhat below the level of the undoped material, as illustrated by Curves C and D. These results are also somewhat surprising since molybdenum trioxide should boil off the surface readily at this temperature, thereby enhancing mass loss. Some reasoning to possibly explain the behavior shown by tungsten and molybdenum additives under these particular test conditions will be presented in a later section.

6. C. 3 Gas Analysis

Gas samples were taken by opening a valve to the gas sample vessel during the oxidation or by collecting all of the gases in a liquid helium trap. No differences were found in results obtained by the two methods.

Table XIII shows the mass spectrometer results on typical experiments with the undoped core material. Both CO and CO₂ were formed in the reaction. No evidence was found for the existence of (CN)₂ when air was used as the test gas. Two general mechanisms have been proposed for the reaction⁽⁶⁾: (1) CO is the primary reaction product with CO₂ forming by a gas phase or surface reaction of CO with oxygen and (2) CO₂ is the primary reaction product with CO forming by CO₂ reacting with the graphite surface.

An analysis of the results in Table XIII suggests that CO is the primary reaction product. When air is used to oxidize the graphite, the CO/CO₂ ratio is greater than unity. When oxygen is used at the higher pressure of 9.5 Torr, the CO/CO₂ ratio is less than 1/3. At an oxygen pressure of 5 Torr, a ratio of 1/2 is found. This dependence of the ratio on the oxidizing gas and upon pressure would be expected if CO was the primary reaction product. The gas phase oxidation of CO to CO₂ is favored in O₂ and at higher oxygen pressures, thus acting to decrease the CO/CO₂ ratio.

It is concluded that CO is the primary reaction product at 1200°C for pressures of 5 to 9.5 Torr in both air and oxygen. The CO₂ is formed by gas phase oxidation or by surface reaction on the walls of the ceramic tube. High flow velocities and low oxygen concentrations favor the formation of CO in the final gas mixture.

Table XIII

Gas Analyses - Oxidation of Reference Graphite

Oxidizing Conditions			Oxidation Rate	Gas Analyses - Volume Per Cent						
Gas	Temp. (°C)	Press Torr	Flow Rate Atoms O+N/sec	Atoms C/cm ² -sec	CO ₂	CO	O ₂	N ₂	H ₂	Ar
O ₂	1200	9.5	8.95×10^{19}	2.42×10^{19}	15.48	4.05	78.87	0.67	0.93	--
O ₂	1200	9.5	9.3×10^{19}	1.98×10^{19}	15.72	2.06	79.93	1.41	0.88	--
O ₂	1200	9.5	1.12×10^{20}	2.82×10^{19}	14.30	4.47	80.06	0.31	0.86	--
O ₂	1200	9.5	1.23×10^{20}	3.24×10^{19}	13.49	4.46	80.90	0.30	0.85	--
O ₂	1200	5	4.98×10^{19}	1.27×10^{19}	14.55	7.47	76.47	0.71	0.80	--
Air	1200	5	1.80×10^{19}	6.85×10^{17}	2.84	--	16.96	79.22	0.04	0.94
Air	1200	5	5.10×10^{19}	2.95×10^{18}	2.08	3.22	16.13	77.59	0.05	0.93
Air	1200	9.5	8.52×10^{19}	6.29×10^{18}	0.54	1.05	19.22	78.23	0.04	0.92
Air	1200	9.5	9.08×10^{19}	6.29×10^{18}	3.01	3.41	15.60	77.03	0.03	0.92
Air	1200	9.5	1.36×10^{20}	8.82×10^{18}	0.95	1.42	14.17	82.41	0.06	0.99

6. D Discussion of Results

Low pressures and high flow rates were used in the oxidation studies in an effort to simulate to some degree the conditions a graphite surface might encounter during certain phases of high velocity re-entry into the earth's atmosphere. Due to the low system pressure employed, the rarefied upper region of the atmosphere would be simulated better than the denser lower regions. The actual gas flow velocities were also very much lower than those which would be initially encountered during a hypersonic re-entry from a degenerating orbit. By the time the body velocity would have diminished to the equivalent 400-500 cm/sec. speed of the molecules through the test apparatus, the body in question would have descended to the high density portion of the lower atmosphere. Therefore, the simulation to the actual environmental conditions which could affect the graphite surfaces of a nuclear reactor is not exact. However, the fact that a flow system is employed for testing will furnish comparative information of a qualitative nature on the behavior of different composition materials exposed under identical conditions.

Since the gas velocities are subsonic, and the mass flow is low, there will be no shock wave generated at the leading edge of the specimen. The molecular collisions will be direct, similar to those in the free-molecule flow regime at high altitude, and a simple mechanical approach to energy conversion may be utilized. It would be expected on this basis that surface chemical reaction rates would be the controlling factor in determining oxidation rates, rather than a gas boundary diffusion control. If this is true, then the reaction should be dependent on surface temperature and pressure within fairly wide ranges. This is indeed the case illustrated by the data gathered in this work. The results indicate that, under any conditions of pressure and temperature employed, the reaction is rate controlled by chemical combination and not by diffusion behavior of reactants or products passing through the gas layer adjacent to the solid surface.

It would be interesting to consider what oxidation behavior might be encountered at temperatures higher than those employed in this work, since peak re-entry surface temperatures for small particles can easily exceed the 1200°C value used here. The

temperature limitation of the present apparatus is approximately 1500°C and some data obtained at this temperature indicate the reaction still to be under chemical rate control. Extrapolation of the data shown in Figures 20-21 to temperatures in the neighborhood of 2200°C would show intersection with the maximum theoretical rate predicted by the kinetic theory of gases. It does not seem possible that such would be the case and there would likely be a change in the slope of the $\log dn/dt$ versus $1/T$ curves somewhere between 1500°C and 2200°C which would provide a flattening effect and keep the reaction rates at some percentage considerably less than the theoretical. At 1200°C it was calculated that the actual rates were somewhere around 1 - 2% of the theoretical. It would be informative to know just how high the rates could go as a function of increased temperature before the peak is reached. Modifications are planned to the present equipment to extend the operating temperature range above 2000°C . When the modifications are completed, attempts will be made to obtain reliable data in the desired temperature range.

The anomaly in the results of the oxidation tests on graphite base materials containing two levels of tungsten and molybdenum additions cannot be adequately explained at the present time. These data also conflict with information generated in Rymer's program on the same materials, results on which have been reported in a previous section. Rymer's data indicate a direct increase of the oxidation rate with the type and amount of additive incorporated. This would be expected on the basis of theoretical analysis. The oxide of molybdenum is highly volatile at the 1200°C test temperature and the oxide of tungsten has a high vapor pressure, being close to its melting point of approximately 1400°C . It can be shown from thermodynamical considerations that both molybdenum carbide and tungsten carbide should preferentially oxidize at 1200°C in a system containing graphite, carbide, and excess oxygen. This should lead to higher mass loss rates because of the complexing effects of the metal ions with carbon and/or oxygen atoms. This was found to be the case in both studies for the 1 w/o tungsten addition, where the oxidation rate was significantly increased. However, in this study the 5 w/o tungsten addition decreased the oxidation rate below that of the reference material. Likewise, both the 1 w/o and 5 w/o molybdenum additions decreased

the oxidation rate below that of the reference material. In Rymer's study all these additions increased oxidation rates considerably.

A careful survey of the design of the two oxidation apparatus and the technique of the test methods used revealed that the only difference was in the actual flow velocity of the gas molecules past the specimen surface. The flow velocity in this study was about 1/3 of that in the other. It is conceivable that the flow velocity per se, irrespective of the total mass flow, has an important bearing on removal of the combustion products from the reacting surfaces. A lower velocity may not tend to sweep away the products by a pressure effect, whereas a higher velocity may accelerate removal. A limiting case of low velocity would be a static system where buildup of combustion products on or near the surface could impede the transport of reactant to the surface, thus inhibiting the reaction. It is true that one would not expect flow velocity to have such a significant effect in a system operating at such low pressures, since the reduced pressure would facilitate removal of products from the surface. However, there does not appear to be any other cause at the present time which can furnish a reasonable explanation for the differences in results obtained in the two independent studies.

6. E Conclusions

The general conclusions drawn from the fundamental oxidation study by E. A. Gulbransen are as follows:

1. The primary oxidation reaction of reactor core graphite at 1200°C in the low pressure range is formation of CO at the gas-solid interface. The adsorption mechanism at the surface is proposed as the rate-controlling step.
2. CO₂ can be formed by the secondary gas phase reaction of excess oxygen with the CO generated at the surface in the primary reaction.
3. The oxidation rate, being chemically controlled by reaction at the surface, is dependent on temperature. Arrhenius plots show an exponential dependence on temperature up to at least 1200°C.
4. The oxidation rate is somewhat dependent on pressure within the range 5 - 9 Torr, being greater at the higher pressure.

5. Data on weight gain versus time at 1200°C show linear relationships, indicating an apparent zero order reaction dependent on time of exposure and not on concentration of reactants or products. This would be expected in a high velocity flow system with an excess of reactant present.

6. The oxidation rate of the undoped reference graphite is significantly increased by the addition of 1 w/o tungsten in the form of tungsten carbide. An addition of 5 w/o tungsten appears to decrease the oxidation below that of the undoped material.

7. Both the 1 w/o and 5 w/o molybdenum additions decrease the oxidation resistance below that of the undoped material.

8. The differences among the data obtained in this study and those in Rymer's concurrent study possibly may be explained on the basis of different gas flow velocities in the two systems.

7. Conclusions and Recommendations

The conclusions of the additive screening study, based on the data obtained from experimental investigations, may be summarized as follows:

1. The refractory hard metals (carbides, borides, nitrides, and silicides) were capable of increasing the strength of unfueled NERVA graphite matrix material in the range from room temperature to above 4000°F.

2. Only small quantities of additives (approximately 1% by weight) were needed to cause significant strengthening when present in the graphite matrix as a uniformly dispersed fine powder. No difficulty was encountered in the fabrication and processing of materials containing up to 5 w/o additives, and the normal procedures could be used.

3. Mechanical property tests (tensile strength and flexural strength) showed significant increases as a result of incorporating certain additives in an unfueled matrix structure. The carbides of tungsten, molybdenum, and vanadium exhibited the most pronounced tendency to maintain a consistent strengthening up to 4000°F. The nitrides, borides, and silicides generally increased the strength at room and moderately elevated temperatures, but were not as effective as the carbides or rhenium at the highest temperature.

6. Tensile strengths of unfueled core material were increased from 15% - 50% and flexural strengths from 10% - 30% depending on the additive and exposure temperature considered.

7. Generally, the incorporation of 5 w/o addition did not greatly improve mechanical properties over the 1 w/o addition. There is probably an optimum composition which will produce the maximum strengthening, but this would have to be determined by more detailed study.

8. It was possible to increase oxidation rates of unfueled core material significantly by the use of certain additives. The incorporation of 1-5 w/o of molybdenum carbide, vanadium carbide, and rhenium metal was capable of more than doubling the oxidation rate of unfueled reference material at the pressure, temperature, and flow rate studied. A 5 w/o tungsten carbide addition increased the oxidation rate by 50%.

9. Nitrides and silicides generally increased the oxidation rate of unfueled materials, but were not as effective as the best carbides and rhenium metal.

10. The boron-containing additives in most cases greatly retarded or did not enhance the oxidation rate of unfueled materials. The tungsten boride addition was the one exception in behavior.

11. The incorporation of 5 w/o of additive further enhanced the oxidation burnup in most cases, but not in proportion to the amount of additive present. There was usually a small but measurable increase in oxidation. The tungsten carbide addition was one exception where the higher addition caused a considerable increase in oxidation.

12. Sensitization drastically reduced the mechanical properties of unfueled materials at all test temperatures. In some cases the strengths fell below that of the reference material. Sensitization had no effect on the mechanical properties of unfueled reference material.

13. In the few tests conducted, sensitization tended to either raise or lower the oxidation rate of unfueled materials containing additives. In the case of tungsten carbide the increase was better than 50%, while in the case of molybdenum carbide, no effect was noted. Sensitization of material containing niobium carbide produced about a

20% increase in the oxidation rate for a 1 w/o addition, but a 30% decrease for a 5 w/o addition. Sensitization had no effect on the oxidation rate of unfueled reference material.

14. The fueled graphite reference material had lower tensile strengths at 4000°F than the unfueled reference material. At lower temperatures the strengths were comparable.

15. Of the five additives incorporated in the fueled material, only the 5 w/o molybdenum carbide addition caused any significant increase in the 4000°F tensile strength. Apparently, the weakening effect of the large uniformly dispersed fuel particles negated the strengthening effect of the additives observed in the unfueled materials.

16. The fueled graphite reference material had consistently lower flexural strength at all temperatures than the unfueled reference material.

17. The fueled graphite material containing selected additives exhibited the same or lower flexural strength as the fueled reference material at the 4000° test temperature. At lower temperatures the strengths were comparable.

18. Sensitization drastically lowered the tensile and flexural strengths of fueled material and additive-fuel material at high temperatures.

19. Based on a normalizing of area and density factors, the oxidation rate of the fueled reference material was nearly 50% greater than that of the unfueled reference material. This result indicates that the fuel itself is a very effective additive from the standpoint of increasing oxidation rates.

20. The oxidation rate of fueled reference material was further increased by the addition of selected additives, (Mo_2C , WC, VC, and Re), the resulting compositions providing the highest oxidation rates of any of the materials tested. For example, the 5 w/o tungsten carbide fueled material exhibited an oxidation rate triple that of the unfueled reference material and double that of the fueled reference material.

21. The effect of additives in fueled materials was primarily an enhancement of oxidation rates, with little positive effect being noted on mechanical properties.

The above conclusions indicate that additives are more effective in the unfueled materials than in the fueled compositions from the standpoint of strengthening effects from normal processing treatments. The effects of additives on oxidation characteristics are

beneficial for both fueled and unfueled materials from the aspect of increasing burnup of re-entering graphite particles. Sensitization would be a desirable treatment prior to primary destruct since it considerably weakens the fuel material and also increases the burnup rate. To determine in a more conclusive manner whether the most promising additives could offer real advantages in core applications, it is desirable to obtain more detailed test data under a wider variety of conditions than was possible in the initial screening study.

First, it is necessary to consider the selection of additives for more detailed study. If the mechanical properties and oxidation rates of all the unfueled materials are compared, there are four additives which exhibit favorable combinations of desirable properties. These are rhenium metal and the carbides of tungsten, molybdenum, and vanadium. It is believed that sufficient promise is shown by these additives to make a more detailed investigation of mechanical properties and oxidation behavior desirable. Therefore, one purpose of the follow-on program would be to further delineate the oxidation properties as a function of temperature, pressure, flow rate, etc. and the mechanical properties as a function of temperature. Another purpose of testing would be to determine the physical property behavior of the additive-bearing materials as a function of temperature. For this purpose, it is suggested that a few thermal conductivity and thermal expansion tests be made on selected fuel materials containing additives.

Second, selection of a few materials must be made from the broad classes of materials available for testing. Since a reasonable screening has been performed in the first phase of work, there appears to be no need to continue study of unfueled materials at this time, at least as far as the flight safety aspects of additive use are concerned. Therefore, it is suggested that fueled reference material and four fueled-additive materials comprise the entire range of test compositions. For maximization of effects, it is further recommended that only the maximum additive contents be used for any composition previously produced.

Another equally important objective of the second phase of work is to determine the destruct behavior of selected additives under simulated flight conditions in an operating reactor. To accomplish this goal, two types of experimental studies will be conducted:

1. Arc plasma wind tunnel tests
2. Chemical destruct tests

Details of these procedures will be discussed in the next section which deals with the conduct of the future program.

8. Future Program

The detailed study program for the next five months will consist of the efforts listed below. Specimen preparation is underway at the present time to permit initiation of the test work by June 1, 1963.

1. Oxidation studies in a flow system will be continued by G. Rymer in the Astronuclear Laboratory. Fuel compositions to be tested are reference, 5 w/o VC, 5 w/o WC, 5 w/o Mo_2C , and 1 w/o Re. Temperatures will be 1000°C and 1400°C at 0.1 mm pressure to bracket the 1200°C temperature used in the present work. Also, another system pressure at 1200°C will be used to determine the effects of pressure on the oxidation rate. Both sensitized and unsensitized materials will be used.

2. Mechanical property studies (tensile strength and flexural strength in the longitudinal direction) will be performed on the same compositions at temperature from room temperature to 4000°F . A 3000°F temperature point will be included. Triplicate specimens will be run at each test point to furnish a strength value in which reasonable confidence can be placed. A total of 74 tensile specimens and 62 flexure specimens will be tested. Both sensitized and unsensitized materials will be used.

3. Thermal expansion tests on unsensitized materials will be run for the five selected compositions up to 5000°F . Tests will be made in the longitudinal or "a" direction.

4. A few tensile tests in the "c", or transverse, direction will be conducted on the five compositions at room temperature. These will be compared to the longitudinal room temperature values to help determine degree of anisotropy.

5. The static elastic modulus will be determined at room temperature, 3000°F and 4000°F for the five compositions in both the sensitized and unsensitized condition.

6. Arc plasma wind tunnel tests will be conducted on the five selected fuel compositions to determine oxidation behavior under simulated re-entry conditions. Comparative tests will also be run on an unfueled reference material and a reference material containing an additive. In addition, a reference fuel material and a fuel-additive composition will be tested in a sensitized condition. Four test points for equipment operation have been chosen. These points will simulate altitude ranges from 150,000 ft. to 260,000 ft. and velocity ranges from 6,000 feet per second to 25,000 feet per second. Four specimens of each composition will be tested at each point to give a good average value for the oxidation rates. A total of approximately 150 tests will be run in this program.

7. Chemical destruct tests will be conducted on the selected additive compositions. Fluorine gas has been shown by extensive testing to be the most promising chemical which could be introduced to the core during a post-operational destruct to accelerate core degradation. Therefore, this gas will be the first investigated to determine if the presence of integral additives in the fuel material will cause an increase in the rate of chemical attack over that of the normal fuel material when surfaces are exposed to fluorine. A few tests of this nature have already been run on specimens of reference unfueled material and unfueled material containing additives. On the basis of weight change it was determined that none of the additives (5 w/o Mo_2C , 5 w/o WC, 1 w/o VC) significantly enhanced the capacity of fluorine to degrade core material. The best of the results (7% weight loss with 5 w/o WC addition) for a 3 1/2 minute run is comparable to results previously obtained consistently with ordinary fueled material. However, the subject will be further studied in sufficient detail to provide a definitive answer to the question of whether additives would contribute to effective core disintegration by a chemical destruct mechanism.

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8. Metallographic analysis will be conducted to a greater extent than in the first phase of work to ascertain the effects of additives and thermal treatments on the microstructure of fueled materials.

9. Chemical analyses will be made on the specimens before and after oxidation tests to determine the degree of reaction of various components.

The above program should furnish sufficient information by the end of the 1963 Contract Year to permit a decision to be made regarding the usefulness of additives in flight safety applications for core destruct. At the present time the indications are that additives will not appreciably strengthen fueled core material as originally believed. At the same time, any weakening effects are probably not sufficient to cause additives to be rejected because of design strength criteria. The additives definitely enhance oxidation of both fueled and unfueled materials. It remains to be seen whether the increase of oxidation rate is sufficient to make the fundamental problem of core destruct simpler. This could be the case if additives caused significantly greater size reduction of particles during re-entry, thereby permitting a larger initial particle size from destruct to be tolerated.

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