2-P

NASA CR-121092

DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS (TASKS VIII, IX, and X)

by

N.J. Fechter and P.S. Petrunich

UNION CARBIDE CORPORATION
Carbon Products Division
12900 Snow Road
Parma, Ohio 44130

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-13211

(NASA-CR-121092) DEVELOPMENT OF SEAL RING CARBON-GRAPHITE MATERIALS (TASKS 8, 9, AND 10) (Union Carbide Corp.) 86 p HC $6.50
CSCL 11A
N73-19481
Unclas
G3/15 65540

84

1. Report No. CR 121092	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle
Development of Seal Ring Carbon-Graphite Materials
(Tasks VIII, IX and X)

5. Report Date
January 1973

6. Performing Organization Code

7. Author(s)
N. J. Fechter and P. S. Petrunich

8. Performing Organization Report No.

9. Performing Organization Name and Address
Union Carbide Corporation
Carbon Products Division
12900 Snow Road
Parma, Ohio 44130

10. Work Unit No.

11. Contract or Grant No.
NAS3-13211

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D. C. 20546

13. Type of Report and Period Covered
Contractor Report

14. Sponsoring Agency Code

15. Supplementary Notes
Project Manager, Lawrence P. Ludwig, Fluid Systems Components Division,
NASA Lewis Research Center, Cleveland, Ohio

16. Abstract

A screening study was conducted to develop improved carbon-graphite materials for use in self-acting seals at air temperatures to 1300° F (704° C). Property measurements on materials prepared during this study have shown that:

1. the mechanical properties of a carbon-graphite material are significantly improved by using a fine milled artificial graphite filler material and including intensive mixing, warm molding, and pitch impregnation in the processing; and
2. the oxidation resistance of a carbon-graphite material is improved by including fine milled boron carbide as an oxidation-inhibiting additive.

These techniques were employed to develop a material that has 10 times more oxidation resistance than that of a widely used commercial grade and mechanical properties that approach those of the commercial grade.

17. Key Words (Suggested by Author(s)) Carbon-Graphite	18. Distribution Statement Unclassified-Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 86	22. Price* $6.50

* For sale by the National Technical Information Service, Springfield, Virginia 22151

NASA-C-168 (Rev. 6-71)

FOREWORD

The work described herein was conducted at the Parma Technical Center, Carbon Products Division of Union Carbide Corporation, under NASA Contract NAS3-13211. Mr. Lawrence P. Ludwig, Fluid System Components Division, NASA-Lewis Research Center, was the Project Manager. Mr. Leonard W. Schopen, NASA-Lewis Research Center, was the Contracting Officer.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

LIST OF TABLES

LIST OF FIGURES

SECTION I

SUMMARY

The object of this Contract is the development of a carbon-graphite seal ring material having long life at ambient air temperatures up to 1300° F (704° C). Since the material is being developed for use in self-acting seals in advanced gas turbine engines, it must have superior oxidation resistance, high strength and hardness, and good wear resistance. Good wear resistance is necessary because self-acting seals experience limited periods of high speed sliding contact. A high thermal conductivity also is desirable to rapidly dissipate the frictional heat generated during periods of sliding contact.

Topical reports NASA CR-72799 and NASA CR-72986 covered the work done under Tasks I through IV. Tasks I and II included the selection of four carbon-graphite formulations from a total of 12 which were derived from a literature survey and bench-scale tests. Task III covered the manufacture of seal ring bodies from the selected four formulations and resin impregnated versions of three of them. Four of the Task III materials subsequently were selected for characterization during Task IV; three of the materials were found to have oxidation resistances and thermal properties superior to those of a widely used commercial grade, but their strengths and hardnesses were low.

Topical report NASA CR-120955 covered the work done under Tasks V through VII, work which was aimed at improving the strength, oxidation resistance, and uniformity of the materials manufactured during Task III. Such improvements would enable broader applications of the materials. Task V included a screening study from which three approaches were formulated for the manufacture of carbon-graphite seal ring bodies which would possess improved properties. Seal ring bodies were made during Task VI from these three formulations, and the properties of these materials were characterized during Task VII. The improvements in mechanical properties anticipated from the Task V screening study were not realized during Task VI because of processing problems encountered during scale-up in material size.

This Topical Report covers the work done under Tasks VIII, IX, and X of this Contract. Twelve material subsystems were processed during the Task VIII screening study to determine methods for improving the strength, hardness, processibility, uniformity, and oxidation resistance of the materials manufactured during Tasks III and VI. The Task VIII screening study was conducted with large size (5-inch (12.7 cm) diameter) compacts to reduce the possibility that scale-up problems would occur later. The five materials from Task VIII with the best mechanical properties were selected for oxidation testing and examination by photomicrograpy during Task IX. Four approaches for the manufacture of improved seal ring carbon-graphite bodies were selected during Task X.

By using fine-milled artificial graphite as the major filler component, incorporating intensive mixing and pitch impregnation as a part of the processing, and adding boron carbide to the mix, we were able to produce carbon-graphite materials which exhibited improved material properties. These techniques were employed to produce the SS-56P-121 material, which was the best material developed for meeting the goal of this Contract. The 2200° C baked SS-56P-121 material contains a filler system consisting of fine-milled Union Carbide Corporation CHP artificial graphite (80 pbw (parts by weight)) and Commercial Solvents Corporation Thermax furnace black (20 pbw). The material is bonded with Barrett No. 30 medium pitch (70 pph (parts by weight per hundred parts filler)), and it contains a 7.5 pbw addition of fine-milled boron carbide. Pitch impregnation is included in the processing prior to final baking, and, finally, the material is impregnated with the No. 121 oxidation-inhibiting treatment.

The SS-56P-121 material possessed the best combination of properties for meeting the goal of this Contract. The SS-56P-121 material was significantly more oxidation resistant than all the materials except one, and that material would be too soft for use in self-acting seals. Based on measurement of the time required to produce a five percent weight loss when exposed to 1300° F (704° C) air, we found that the boronated SS-56P-121 material was approximately 10 times more oxidation resistant than a widely used commercial grade. Except for two other materials which were significantly less oxidation resistant, the SS-56P-121 material was significantly stronger and harder than any of the other materials developed under the scope of this Contract. The mechanical properties of the SS-56P-121 material approached those of the widely used commercial seal ring grade.

The SS-56P-121 material was selected during Task X as one of the four material formulations for the manufacture of improved seal ring carbon-graphite materials. The second formulation was the same as that used for the SS-56P-121, except that the boron carbide addition was increased to 10 pbw. Two modifications of a previously produced phenolic resin bonded material, containing "graphite" fibers as a minor filler component, were selected as the third and fourth formulations. The work done during Task VIII had shown that poor mechanical properties result when a pitch binder and intensive mixing are used to produce a material which contains "graphite" fibers.

SECTION II

INTRODUCTION

Introduction of the gas turbine engine has produced sealing problems so severe that carbon-graphite is one of the few engineering materials which can meet the requirements of this application. Operating conditions will become more severe as gas temperatures and seal sliding speeds increase. Increased temperatures result from the higher flight speeds or higher gas temperatures used to improve engine efficiency; increased seal sliding speeds result from the use of larger engines. Contact type seals which incorporate carbon-graphite seal rings are used in many current gas turbine engines; however, the limited pressure, speed, and temperature capability of the contact seal restricts this use to operation below 125 psi (86 N/cm^2) sealed pressure differential, 350-ft/sec. (107 meter/sec.) sliding speed, and 800° F (427° C) seal gas temperature.(1)* For more severe operating conditions, labyrinth seals are used. The labyrinth seal systems have higher gas leakage than contact seals, and, therefore, contribute to easier passage of debris and to greater losses in engine efficiency.

Recent studies have resulted in the production of a face seal with self-acting lift augmentation. Since this seal operates without rubbing contact (except at start and stop), it has higher pressure, speed, and temperature capability than a conventional face contact seal. For this new generation of seals, pads are machined on the seal face which, during engine operation, act as a thrust bearing and cause the seal to lift off the seal seat and ride on a thin gas film.(2) The seal with self-acting lift augmentation ideally will experience mechanical wear only during start-up and shut-down of the engine. However, momentary periods of high speed sliding contact may occur because of the close dimensional tolerances associated with the thin gas films.(3) Therefore, the importance of wear resistance cannot be neglected when a carbon-graphite formulation is developed for use as a self-acting seal ring material.

---

* Denotes Reference Number

High hardness, strength, and modulus, together with the proper impregnants and mating materials, are necessary for products which will be used as wear resistant, carbon-graphite seal rings.(4) Increased oxidation resistance will become a major requirement of carbon-graphite seal rings as engine gas temperatures rise to 1200° F (649° C) and above. Development of improved carbon-graphite seal ring materials which can operate in ambient air temperatures up to 1300° F (704° C) will make feasible seal designs which will contribute to improvements in engine performance.

Conventional carbon-graphite seal ring materials are prepared by mixing selected sizes and types of carbon and graphite fillers with a binder such as coal tar pitch. The mixtures are formed into compacts and baked to temperatures which are adjusted to produce the desired properties of the finished material. Usually, the finished carbon-graphite seal ring contains additives or impregnants which help the seal to meet particular performance requirements (e. g. , oxidation resistance). Specific raw materials or processing techniques are employed to obtain desired properties of the finished carbon-graphite material. Detailed descriptions of the raw materials and processes employed specifically for the preparation of carbon-graphite seal rings are not available in the literature.

The final phase of the work that is reported herein is based on prior work done under Tasks I through VII. This prior work has been described in the following reports:

1. NASA CR-72799(5) (Tasks I and II)
    a. Literature search
    b. Formulation of 12 material systems
    c. Optimization of 12 material systems through material/process subsystem studies (47 formulations)
    d. determination of properties of the 12 optimized material systems (strength, hardness, density, and oxidation resistance)
    e. Selection of four material systems for further seal ring manufacture.

2. NASA CR-72986(6) (Tasks III and IV)

a. Manufacture of seal ring bodies from selected four material systems and three additional material systems that had resin impregnation

b. Determination of material properties.

3. NASA CR-120955(7) (Tasks V, VI, and VII)

a. Further improvement of material systems based on results of Tasks I through IV; manufacture and screen testing of material systems

b. Manufacture of seal ring bodies; three material systems

c. Determination of material properties.

The general overall objective of this final phase was to maintain the improved oxidation resistance obtained in the prior work but to obtain increased material hardness, strength, and improved processibility. The specific objectives were to; (a) determine if mechanical properties can be improved by using fine-milled graphite, intensive mixing, warm molding, and pitch impregnation; and (b) evaluate the effect of boron carbide addition on oxidation resistance.

Large 5-inch (12.7 cm) diameter compacts were processed from 12 approved material subsystems during Task VIII. The five materials which demonstrated the best mechanical properties were selected for structural examination and oxidation testing during Task IX. A review of the work done during Tasks I through VI and the experience gained under Tasks VIII and IX were used during Task X to select four approaches for the manufacture of improved seal ring carbon-graphite bodies.

SECTION III

CONCLUSIONS

1. The mechanical properties of a pitch bonded carbon-graphite material are significantly improved by fine milling the artificial graphite filler, using multiple extrusion as an intensive mixing operation, warm molding the green compacts, and incorporating pitch impregnation as a part of the processing of the material prior to final baking.

2. The oxidation resistance of a carbon-graphite material is significantly improved by including fine-milled boron carbide as an oxidation-inhibiting additive. The greatest increases in oxidation resistance are obtained by baking the boronated material to a final temperature just below the melting point of the boron carbide.

3. The material manufactured from subsystem SS-56P-121 is the best thus far developed under the scope of this Contract for meeting the requirements of a self-acting seal material. The filler system of the pitch bonded SS-56P-121 material is fine-milled artifical graphite (80 parts by weight) and furnace black (20 parts by weight). This 2200° C final baked material contains fine-milled boron carbide (7. 5 parts by weight) as an oxidation-inhibiting additive and includes in its processing intensive mixing, warm molding, and pitch impregnation prior to final baking. Material prepared from SS-56P-121 is 10 times more oxidation resistant than a widely used commercial seal ring grade and its mechanical properties approach those of the commercial grade.

SECTION IV

MATERIALS/PROCESS SCREENING STUDY (TASK VIII)

A. Identification of Twelve Approved Material Subsystems

The carbon-graphite seal ring materials developed during Tasks I through VII(5, 6, 7) of this Contract (Tables I and II) have oxidation resistances which are several times greater than that of a widely used commercial grade, but their flexural strengths are approximately half that of the commercial grade. Since these oxidation resistant carbon-graphite materials were developed for use as self-acting seal rings which normally employ metal retaining bands, the strengths of these materials were judged acceptable. Erosion resistance may also be an important requirement for self-acting seal materials. Debris passing through the gas film formed between the sealing dam and the seat is responsible for the erosion of the seal face. Increases in strength would mitigate the necessity of metal retaining bands, and increases in hardness would improve erosion resistance. Since these improvements would enable broader application of the carbon-graphite seal ring materials, a screening study was conducted during Task VIII to find possible methods for improving the strengths, hardnesses, uniformity, and oxidation resistances of the materials manufactured during Tasks III and VI. (6, 7)

The Task VIII screening study called for the manufacture of materials from 12 material subsystems approved by the NASA Project Manager. Selection of the 12 material subsystems was based on a review and analysis of the previous Contract work. The 12 subsystems were believed to be the most promising approaches for improving the properties of the seal ring materials manufactured during Tasks III and VI. (6, 7) Table I displays the compositions of the materials manufactured during Task III(6) and Table II presents the compositions of those manufactured during Task VI. (7) The compositions of the 12 subsystems approved for processing during Task VIII are presented in Table III.

TABLE I

Material Formulations Developed Under Tasks I Through IV

Formulation No.	Base Material			Impregnants	
	Particulate Solid Raw Material	Additive	Binder Raw Material	Resin Impregnant*	Oxidation Inhibiting Treatment**
1	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	---	No. 30 Medium Pitch (60 pph)	----	----
2	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	Glassy Carbon(5 pbw)	No. 30 Medium Pitch (60 pph)	----	----
3	CHP Artificial Graphite (80 pbw) Thermax (20 pbw)	---	Bakelite BRP-5095 Phenolic Resin (58 pph)	----	----
4	CHP Artificial Graphite (80 pbw) WCA Fibers (20 pbw)	---	Bakelite BRP-5095 Phenolic Resin (67.5 pph)	----	----
1X	Formulation No. 1 Base Material			Bakelite BRP-5095 Phenolic Resin	----
2X	Formulation No. 2 Base Material			Bakelite BRP-5095 Phenolic Resin	----
4X	Formulation No. 4 Base Material			Bakelite BRP-5095 Phenolic Resin	----
1X-121	Formulation No. 1 Base Material			Bakelite BRP-5095 Phenolic Resin	No. 121 Treatment
2X-121	Formulation No. 2 Base Material			Bakelite BRP-5095 Phenolic Resin	No. 121 Treatment
3 -121	Formulation No. 3 Base Material			----	No. 121 Treatment
4X-121	Formulation No. 4 Base Material			Bakelite BRP-5095 Phenolic Resin	No. 121 Treatment

---

Note: Final Bake Temperature = 2800°C.
Proportions are parts by weight (pbw).
Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials.

* Dissolve resin in an equal weight of acetone, impregnate 1000°C baked compacts, pressure cure at 150°C, rebake to 1000°C, and final bake to 2800°C.

** Impregnate with oxidation inhibiting treatment after desired configuration has been finish machined from 2800°C baked stock.

TABLE II

Material Formulations Developed Under Tasks V Through VII

Formulation No.	Base Material			Impregnants	
	Particulate Solid Raw Material	Binder Raw Material	Baking Procedure	Resin Impregnant	Oxid. Inhibiting Treatment ***
1	CHP Artificial Graphite (80pbw) Thermax (20 pbw)	No. 30 Medium Pitch (60pph)	Bake Green Compacts at 1000° C and Final Bake to 2800° C	----	----
5	CHP Artificial Graphite (80pbw) Thermax (20 pbw)	Bakelite BRP-5095 Resin (58 pph)	Pressure Cure Green Compacts at 150° C, Pressure Bake to 550° C, Bake to 1000° C, and Final Bake to 2800° C	----	----
6	CHP Artificial Graphite (80pbw) WFA Graphite Fibers (20 pbw)	Bakelite BRP-5095 Resin (70 pph)	Same as that used for Formulation No. 5	----	----
1Z	Formulation No. 1 Base Material			Furfuryl Alcohol (50pbw) Bakelite BRP-5095 Resin (35pbw)*	----
6Y	Formulation No. 6 Base Material			Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)**	----
1Z-121	Formulation No. 1 Base Material			Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)*	No. 121 Treatment
5-121	Formulation No. 5 Base Material			----	No. 121 Treatment
6Y-121	Formulation No. 6 Base Material			Furfuryl Alcohol (50 pbw) Bakelite BRP-5095 Resin (35 pbw)**	No. 121 Treatment

Note: Final Bake Temperature = 2800° C.
Proportions are parts by weight (pbw).
Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials (pph).

* Impregnate 2800° C baked compacts with resin solution, pressure cure at 150° C, rebake to 1000° C, and final bake to 2800° C.

** Impregnate 1000° C baked compacts with resin solution, pressure cure at 150° C, rebake to 1000° C, and final bake to 2800° C.

*** Impregnate with oxidation-inhibiting treatment after desired configuration has been finished machined from 2800° C baked stock.

TABLE III

Identification of Material Subsystems SS-52 to SS-63

Subsystem No.	Base Material Particulate Solid Raw Material	Binder Raw Material	Binder Level	Additive per 100 pbw Base Material
SS-52	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Medium Pitch	30 pph	----
SS-53	"	"	45 pph	----
SS-54	"	"	60 pph	----
SS-55	"	"	*	B_4C (5 pbw)
SS-56	"	"	*	B_4C (7. 5 pbw)
SS-57	"	"	*	B_4C (10 pbw)
SS-58	Fine Milled CHP Artificial Graphite (80 pbw) & WFA Graphite Fibers (20 pbw)	No. 30 Medium Pitch	40 pph	----
SS-59	"	"	55 pph	----
SS-60	"	"	70 pph	----
SS-61	"	"	**	B_4C (5 pbw)
SS-62	"	"	**	B_4C (7. 5 pbw)
SS-63	"	"	**	B_4C (10 pbw)

Note: Proportions are parts by weight (pbw).
Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials (pph).
Boron carbide additions blended with mixes of base materials just prior to molding "green" compacts.

* Binder level to be based on the results of the analysis of the materials manufactured from subsystems SS-52, SS-53, and SS-54.

** Binder level to be based on the results of the analysis of the materials manufactured from subsystems SS-58, SS-59, and SS-60.

Subsystems SS-52, SS-53, SS-54, SS-58, SS-59, and SS-60 will be baked to a final temperature of 2800° C. The other six materials may be baked to lower final temperatures.

All 12 of the material subsystems presented in Table III specify fine-milled CHP artificial graphite as the major filler component. The fine-milled graphite was employed in an attempt to improve the strength of the seal ring carbon-graphite materials. Table IV displays the particle size distribution of the fine-milled CHP graphite as determined by the MSA-Sedimentation Particle Size Analysis. The fine milling reduced the average particle size of the graphite from 25μ (micron) to approximately 4μ. This reduction in particle size doubled the surface area of the CHP graphite.

Multiple (three passes) extrusion was included as a part of the mixing operation for the 12 subsystems presented in Table III. The multiple extrusion was designed to give a better dispersion of the pitch binder around the particulate filler materials, thereby yielding stronger and more uniform pitch bonded materials than those manufactured during Tasks III and VI.(6, 7) The multiple extrusion technique should permit the use of low binder levels and thereby reduce the disparity in voids produced by excess binder. Disparate voids produce stress risers which cause failure of the material at low stress.

Except for the use of the fine-milled boron carbide and the Grade VFA and Grade WFA fibers, all the materials listed in Tables I, II, and III were manufactured from particulate and binder raw materials whose properties had been determined during Task I.(5) The properties determined for the raw materials also are included in this section of the report. Descriptions of the test procedures used for the property determination are presented in Appendix I.

The fine-milled boron carbide was purchased from Atomergic Chemetals Division of Gallard-Schlesinger Chemical Corporation. The particle size of the boron carbide, which was specified as 1000 mesh by the supplier, was measured by using a Fisher Subsieve Sizer. An average particle size of 1.5μ was determined for the fine-milled boron carbide by using the Fisher Subsieve Sizer, but examination of the material under a microscope showed that it contained many agglomerates. Due to the presence of the agglomerates, only approximately one-half of the fine-milled boron carbide would pass through a 325 mesh (43μ) Tyler screen.

TABLE IV

MSA-Sedimentation Particle Size Analysis

Particle Size Microns-Diameter	Percent by Volume Greater Than Size Regular CHP Artificial Graphite	 Fine Milled CHP Artificial Graphite
100. 0	0. 0	0. 0
80. 0	0. 0	0. 8
60. 0	8. 0	0. 8
50. 0	15. 0	1. 5
40. 0	22. 0	1. 5
35. 0	31. 0	1. 5
30. 0	40. 0	1. 5
25. 0	49. 0	3. 8
20. 0	56. 0	3. 8
18. 0	61. 0	---
16. 0	66. 0	---
15. 0	----	3. 8
14. 0	67. 0	---
12. 0	70. 0	---
10. 0	73. 0	18. 0
8. 0	79. 0	---
6. 0	86. 0	---
5. 0	92. 0	44. 0
4. 0	95. 0	---
3. 0	97. 0	61. 0
2. 0	100. 0	---
1. 0	100. 0	96. 0
0. 8	100. 0	100. 0

CHP Artificial Graphite	Helium Density (g/cc)	B. E. T. Surface Area (m^2/g)
Regular	2. 22	6. 7
Fine-Milled	2. 24	14. 6

Grade VFA carbon fibers and Grade WFA "graphite" fibers are produced by pyrolyzing continuous filament rayon yarn which is subsequently chopped to the desired lengths. Properties of these two fiber materials were obtained from "Union Carbide Corporation Technical Information Bulletin No. 456-213 cj." The brochure lists a density (water immersion) of 1.8 g/cc and a weight percent ash of 0.8 for the Grade VFA carbon fibers. Grade WFA "graphite" fibers are reported to have a density (water immersion) of 1.4 g/cc, a surface area of 2 m^2/g, and a weight percent ash of 0.1.

Properties previously determined for the other raw materials are displayed in the six listings that follow.

1. Union Carbide Corporation Grade CHP Artificial Graphite

Helium Density = 2.22 g/cc

Surface Area = 6.7 m^2/g

Screen Analysis

On 35 mesh = 0%
On 65 mesh = 0%
On 100 mesh = 0%
On 150 mesh = 0.08%
On 200 mesh = 3.30%
On Pan = 96.62%

Chemical Analysis

% Ash = 0.066
% Moisture = 0.039

Emission Spectrographic Analysis (Semi-Quantitative)

Al = 7 ppm
Ti = 37 ppm
V = 23 ppm
Fe = 44 ppm
Ni < 5 ppm
Cr < 5 ppm
Si = 60 ppm
Ca = 162 ppm
Mg < 5 ppm
Pb < 5 ppm
Sn < 5 ppm
Ag < 5 ppm
B = 6 ppm
Na < 5 ppm
Cu < 5 ppm

2. Commercial Solvents Corporation Thermax Furnace Black

Helium Density = 1.84 g/cc

Surface Area = $8.1\ m^2/g$

Screen Analysis*

On 35 mesh = 3.97%
On 65 mesh = 36.91%
On 100 mesh = 15.74%
On 150 mesh = 13.44%
On 200 mesh = 10.84%
On Pan = 19.10%

Chemical Analysis

% Ash = 0.022
% Moisture = 0.027

Emission Spectrographic Analysis (Semi-Quantitative)

Al < 5 ppm
Ti < 5 ppm
V < 5 ppm
Fe < 5 ppm
Ni < 5 ppm
Cr < 5 ppm
Si = 33 ppm
Ca = 11 ppm
Mg = 5 ppm
Pb = 5 ppm
Sn < 5 ppm
Ag < 5 ppm
B = 5 ppm
Na = 23 ppm
Cu < 5 ppm

---

* The presence of aggregates appears to have a significant effect on the results of the screen analysis.

3. Lockheed Company LMSC Glassy Carbon (Ground)

Helium Density = 1.91 g/cc*

Surface Area = 5.6 m^2/g

Screen Analysis

On 35 mesh =	0%
On 65 mesh =	0%
On 100 mesh =	0.41%
On 150 mesh =	18.42%
On 200 mesh =	21.98%
On Pan =	59.19%

Chemical Analysis

% Ash = 0.92
% Moisture = 0.85

Emission Spectrographic Analysis (Qualitative)**

+ Major-	+ Minor-	+ Trace-
←Fe	Mn	Mg→
Cr	Sn→	Ag→
Ni	Si	
	Al	
	Ca	
	Cu	

---

* A prolonged period was required for the Beckman pycnometer to reach equilibrium conditions and, therefore, the results are questionable.

** No standards available to run semi-quantitative analysis.

4. Union Carbide Corporation Grade WCA Graphite Cloth

Helium Density = 1.43 g/cc*

Surface Area = 1.3 m^2/g

Chemical Analysis

% Ash = 0.04
% Moisture = 0.03

Emission Spectrographic Analysis
Semi-Quantitative

Al < 5 ppm
Ti = 5 ppm
V < 5 ppm
Fe < 5 ppm
Ni < 5 ppm
Cr < 5 ppm
Si = 7 ppm
Ca < 5 ppm
Mg < 5 ppm
Pb < 5 ppm
Sn < 5 ppm
Ag < 5 ppm
B < 5 ppm
Na = 13 ppm
Cu < 5 ppm

---

* A prolonged period was required for the Beckman pycnometer to reach equilibrium conditions and, therefore, the results are questionable.

5. Barrett No. 30 Medium Coal Tar Pitch

Helium Density = 1.33 g/cc

Coking Value = 57.4%

Benzene Insoluble = 32.1%

Quinoline Insoluble = 13.1%

Softening Point = 100.3°C

Elemental Chemical Analysis

C = 93.62%
H = 4.29%
O = 1.56%
N = 0.92%
S = 0.44%

Emission Spectrographic Analysis (Qualitative)*

+ Major-	+ Minor-	+ Trace-
	Fe	Mg
	Pb→	Mn
	Si	
	Al	Cu→
	Ca→	
	Ti→	
	Zn→	

Differential Thermal Analysis

Endotherm at 55°C.
Endotherm at 440°C.
Exothermic jump at 535°C. which is coincidental with 3% weight loss.
Exothermic rise maximum at 645°C.

Thermal Gravimetric Analysis

Essentially constant weight to 200°C.
Gradual loss between 200°C and 260°C.
-1% at 260°C.
Increasing rate of loss between 260°C and 335°C
Steady rate of loss from 335°C to 460°C and 605°C to 800°C with a slightly lower rate of loss between 460°C and 605°C.
-10% at 370°C.
Overall loss of 83% at cut off of 800°C

Volume Change After Baking**

$$\frac{\text{1000°C Baked Volume}}{\text{Green Volume}} = 0.871$$

$$\frac{\text{2800°C Heat Treated Volume}}{\text{Green Volume}} = 0.843$$

---

* No standards available to run semi-quantitative analysis.

** Measured for compacts containing 80 pbw CHP graphite, 20 pbw Thermax, and 60 pph No. 30 Med. Pitch.

6. Bakelite BRP-5095 Phenol-formaldehyde Resin

Helium Density = 1.28 g/cc

Coking Value = 65.4%

Elemental Chemical Analysis

C = 75.86%
H = 6.13%
O = 16.80%
N = 2.44%
S = None

Emission Spectrographic Analysis (Qualitative)*

+ Major-	+Minor-	+Trace-	
	←Ca	←Fe	Cu
	Si→	Al	←Ni
	Mg	Cr→	
		Mn→	

Differential Thermal Analysis

Small exotherm at 165°C which is just at the beginning of 5% weight loss.
Very broad exothermic rise beginning at 540°C.

Thermal Gravimetric Analysis

Essentially constant weight to 160°C.
Gradual loss between 160°C and 265°C.
Plateau between 265°C and 370°C at approximately 5% loss.
-10% at 445°C.
Steady loss between 370°C and 540°C.
Increasing rate of loss to 600°C.
Steady loss rate to cut off at 750°C.
Overall loss of 88% at cut off of 750°C.

Volume Change After Baking**

$$\frac{\text{1000°C Baked Volume}}{\text{Green Volume}} = 0.704$$

$$\frac{\text{2800°C Heat Treated Volume}}{\text{Green Volume}} = 0.649$$

---

* No standards available to run semi-quantitative analysis.

** Measured for compacts containing 80 pbw CHP graphite, 20 pbw Thermax, and 58 pph Bakelite BRP 5095 resin.

B. Screen Testing of Approved Material Subsystems

The 12 subsystems listed in Table III were divided into two general classifications, boronated and nonboronated materials. The six nonboronated subsystems were prepared and characterized first to determine the optimum binder levels for the two filler systems being studied. Both filler systems employed fine-milled CHP artificial graphite as the major component (80 pbw) with Thermax furnace black and Grade WFA graphite fibers comprising the two minor filler components (20 pbw). The six boronated materials listed in Table III were to be subsequently prepared by adding fine milled boron carbide to the mixes of the two optimized base materials just prior to the molding of green compacts. Adding the highly abrasive boron carbide as a particulate filler component prior to mixing would have resulted in metal contamination of the boronated materials. The metal particles, which would be picked up during the mixing and milling operations, would act as oxidation catalysts for the carbon-graphite materials.

1. Nonboronated Material Subsystems

The nonboronated materials prepared from subsystems SS-52 through SS-54 and SS-58 through SS-60 were processed according to the following procedure. (The chopped Grade WFA graphite fibers used as the minor filler component for subsystems SS-58 through SS-60 were micromilled prior to blending with the fine milled CHP artificial graphite.)

a) Blend filler raw materials for one hour,

b) Preheat filler and mixer to 150° C, add pitch, and mix filler and binder in a sigma blade mixer for one hour.

c) Remove hot mix from sigma blade mixer and immediately pass it three times through a pellet mill to produce small rods measuring 1/8-inch (0. 32 cm) in diameter by 1/8 to 1/2-inch (0. 32 to 1. 27 cm) in length.

d) Cool pelletized mix to room temperature and micromill.

e) Blend milled material for one hour.

f) Mold the milled material at the desired temperature by using a hydraulic press.

g) Pack green compacts with coke in a sagger, place a layer of charcoal on top of the pack, and bake green compacts to 1000° C using the following schedule: rush to 50° C, 50° C to 500° C at 2.5° C per hour, 500° C to 1000° C at 5.0° C per hour, and hold four hours at 1000° C.

h) Using graphite particles as the packing medium, fire the 1000° C baked compacts to 2800° C in an induction furnace, employing the following schedule: room temperature to 900° C at 400° C per hour, 900° C to 1600° C at 200° C per hour, 1600° C to 2800° C at 300° C per hour, and hold one hour at 2800° C.

All the materials processed during the Task VIII screening study were molded into large compacts measuring 5-inches (12.7 cm) in diameter by 1.4-inches (3.6 cm) thick. These large-size compacts were used for the Task VIII screening study to preclude the type of scale-up problems experienced during Task VI. (7) Processing problems were encountered during Task VI(7) when we attempted to manufacture large 5-inch (12.7 cm) diameter compacts by employing the same processing techniques successfully using during Task V(7) to prepare much smaller compacts (2.5-inch x 1.25-inch x 1.0-inch (6.35 cm x 3.18 cm x 2.54 cm)). Using the large compacts during the Task VIII screening study greatly reduced the possibility of scale-up problems during the manufacture of large (7-12 inches in diameter) seal materials at some later date.

To determine the optimum molding pressures for the materials manufactured from the nonadditive subsystems, we molded a series of compacts for each material at pressures between 5000 psi (3450 N/cm^2) and 30,000 psi (20,670 N/cm^2). The "green" densities of these compacts are displayed in Table V. Some of the compacts were warm molded at 100° C, which is the softening point of the No. 30 medium pitch. The decision as to which materials warranted warm molding was based on the binder levels of the materials. The materials with the highest binder levels were either not warm molded or a second room-temperature molded version was prepared, since there was concern that warm molding would result in such low porosity compacts that they could not be successfully baked. The volatiles must be able to escape from the molded compacts during baking to avoid disruption of their internal structures.

TABLE V

Green Densities of Nonboronated Materials

Subsystem No.	Filler Material	Binder Level	Molding Temperature	Green Density (g/cc) at Following Molding Pressures(psi)					
				5,000	10,000	15,000	20,000	25,000	30,000
SS-52	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	60 pph	100°C	1.680	1.697	1.697	1.697*	-----	-----
SS-53A	"	70 pph	100°C	1.656	1.662	1.663*	1.662*	-----	-----
SS-53B	"	70 pph	Room Temp.	-----	1.545	1.594	1.622	1.638	1.653
SS-54	"	80 pph	Room Temp.	-----	1.534	1.581	1.611	1.623	1.635
SS-58	Fine Milled CHP Artificial Graphite (80 pbw) & WFA Graphite Fibers (20 pbw)	40 pph	100°C	1.607	1.651	*	-----	-----	-----
SS-59	"	55 pph	100°C	1.596	1.642	1.652	1.657	1.657	-----
SS-60A	"	70 pph	100°C	1.618	1.618	1.608	1.610	-----	-----
SS-60B	"	70 pph	Room Temp.	-----	1.488	1.548	1.584	1.604	-----
SS-64	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	45 pph	100°C	1.670	1.728	1.740	1.744	1.747	1.748

Note: All the above materials are bonded with No. 30 medium pitch.

Green densities are the average for two 5-inch (12.7 cm) diameter x 1.4-inch (3.6 cm) thick solid plugs of each material at each molding pressure.

* Green plugs cracked when ejected from mold.

Proportions are parts by weight (pbw)

Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials (pph).

The binder levels listed in Table V for subsystems SS-52 through SS-54 are not the same as those listed in Table III for the same three materials. The binder levels of the three materials were increased when, during primary mixing (sigma blade mixer), the materials appeared (by visual inspection) to be binder deficient. Apparently, the significant increase in surface area resulting from fine milling (Table IV) had greatly increased the binder demand of the CHP artificial graphite. After manufacturing materials from subsystems SS-52 through SS-54, we extended the study of the effect of changes in binder level and molding temperature on material properties by processing the SS-64 material during Task VIII. The binder level of subsystem SS-64 (Table V) was 45 pph, the same level as that initially formulated for the SS-53 material.

All the "green" compacts molded for the nonadditive subsystems (Table V) were processed through final baking to 2800° C. The molding pressure that yielded the highest 2800° C baked density for each material was selected as its optimum molding pressure. The mechanical properties of the compacts prepared at these molding pressures are displayed in Table VI.

Subsystem SS-53A yielded the best carbon-graphite material of those employing Thermax as the minor filler component. The elastic modulus, bulk density, and hardness of the SS-53A material were significantly higher than those of the similar formulation No. 1 material (composition listed in Table I) manufactured during Task III;(6) the flexural strengths of the two materials were identical, however. The formulation No. 1 material, which had been selected as the best material of those manufactured during Task III,(6) had a 2800° C baked bulk density of 1. 707 g/cc, a Rockwell "S" hardness of 80, and an elastic modulus of 1.31×10^6 psi (9.03×10^5 N/cm^2). Because of its increased hardness, the SS-53A material should be a more wear-and erosion-resistant carbon-graphite material than that manufactured from formulation No. 1. The SS-53A material was selected as the base material from which the boronated materials of subsystems SS-55, SS-56, and SS-57 (Table III) would be processed.

TABLE VI

Optimum Molding Pressures and Mechanical Properties of Nonboronated Subsystems

A. Material Compositions

Subsystem No.	Filler Material	Binder Material	Binder Level	Molding Temperature	Optimum Molding Pressure (psi)
SS-52	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Medium Pitch	60 pph	100°C	10,000
SS-53A	"	"	70 pph	100°C	5,000
SS-53B	"	"	70 pph	Room Temp.	30,000
SS-54	"	"	80 pph	Room Temp.	30,000
SS-58	Fine Milled CHP Artificial Graphite (80 pbw) & WFA Graphite Fibers (20 pbw)	"	40 pph	100°C	5,000
SS-59	"	"	55 pph	100°C	15,000
SS-60A	"	"	70 pph	100°C	5,000
SS-60B	"	"	70 pph	Room Temp.	25,000
SS-64	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	"	45 pph	100°C	20,000

Note: Proportions are parts by weight (pbw)

Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials (pph).

B. Material Properties

Subsystem No.	Bulk Density (g/cc)*			Flexural Strength**				Elastic Modulus**				Rockwell "S" Hardness***	
	Green	1000°C Baked	2800°C Baked	(psi) Average	(psi) σ	(N/cm²) Average	(N/cm²) σ	(10^6 psi) Average	(10^6 psi) σ	(10^6 N/cm²) Average	(10^6 N/cm²) σ	Average	σ
SS 52	1.697	1.723	1.786	3350	230	2310	158	1.60	0.03	1.10	0.02	98	1
SS-53A	1.656	1.754	1.829	3810	347	2630	239	1.74	0.08	1.20	0.06	106	2
SS-53B	1.653	1.707	1.777	3610	248	2490	171	1.66	0.04	1.14	0.03	102	2
SS-54	1.635	1.716	1.788	3130	356	2160	245	1.75	0.03	1.21	0.02	104	2
SS-58	1.607	1.513	1.515	850	106	590	73	0.76	0.06	0.52	0.04	23	5
SS-59	1.652	1.592	1.600	2140	373	1470	257	1.29	0.05	0.89	0.03	62	2
SS-60A	1.618	1.596	1.617	2930	486	2020	335	1.48	0.06	1.02	0.04	76	2
SS-60B	1.604	1.533	1.553	2400	421	1650	290	1.23	0.04	0.85	0.03	68	5
SS 64	1.744	1.686	1.732	1830	194	1260	134	1.41	0.04	0.97	0.03	84	1

* Average of measurements made for two 5" (12.7 cm) diameter plugs.

** Average of four tests conducted using 4.5" x 1.0" x 0.5" (11.4 cm x 2.5 cm x 1.3 cm) samples. Flexural samples broken on a 3.0" (7.6 cm) span per ASTM procedure C651-70.

*** R_s Scale = 1/2" (1.3 cm) diameter ball and 100 Kg. maj. load. Two measurements made on each of the four samples.

Subsystem SS-60A yielded the best material of the subsystems employing Grade WFA graphite fibers as the minor filler component. The density, modulus, and hardness of the SS-60A material were higher than those of the similar formulation No. 4 material (composition listed in Table I) manufactured during Task III(6). The flexural strength of the SS-60A material was, however, considerably lower than that of the formulation No. 4 material. Formulation No. 4 yielded a material having a 2800° C baked bulk density of 1.441 g/cc, a flexural strength of 3880 psi (2670 N/cm^2), an elastic modulus of 1.19×10^6 psi (0.82×10^6 N/cm^2), and a Rockwell "S" hardness of 26. The low flexural strengths of the materials manufactured from subsystems SS-58 through SS-60B may indicate that the pitch binder did not adequately wet the graphite fibers or that the fibers may have been so degraded during multiple extrusion that they did not reinforce the compacts. After examining the materials containing fibers and reviewing their physical properties, the NASA Project Manager requested that no further work be done with them; thus, the boronated materials to be manufactured from subsystems SS-61 through SS-63 (Table III) were not produced during Task VIII.

2. Boronated Material Subsystems

Based on the analysis of the nonboronated materials specifying Thermax as the minor filler component, subsystem SS-53A was selected as the best base composition for use in the manufacture of the boronated materials from subsystems SS-55 through SS-57. The latter three subsystems specify fine-milled boron carbide as an oxidation-inhibiting additive. Table VII presents a complete description of the materials manufactured from subsystems SS-53A, SS-55, SS-56, and SS-57. The three materials containing boron carbide were prepared by using the following procedure. (All blending was done in a twin-shell blender equipped with an intensifier bar.)

a) Preblend equal amounts (by weight) of the fine-milled boron carbide and the SS-53A mix for 1/2 hour.

b) Add remaining requirement of the SS-53A mix and blend an additional hour.

TABLE VII

Material Compositions and Properties for Subsystems SS-53A, SS-55, SS-56, and SS-57

A. Material Compositions

Subsystem No.	Base Material		Additive	Molding Pressure (psi)	Molding Temp. (°C)	Final Baking Temp(°C)
	Filler Material	Binder Material				
SS-53A	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Medium Pitch (70 pph)	---	5000	100	2800
SS-55	SS-53A Base Material (100 pbw)		B_4C (5 pbw)	"	"	2200
SS-56	SS-53A Base Material (100 pbw)		B_4C (7.5 pbw)	"	"	"
SS-57	SS-53A Base Material (100 pbw)		B_4C (10 pbw)	"	"	"

Note: Proportions are parts by weight (pbw)

Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials (pph).

Boron carbide addition blended with SS-53A base mix just prior to molding "green" compacts.

B. Material Properties

Subsystem No.	Bulk Density (g/cc)*			Flexural Strength**				Elastic Modulus**				Rockwell "S" Hardness ***	
				(psi)		(N/cm^2)		(10^6 psi)		($10^6 N/cm^2$)			
	Green	1000°C Baked	Final Baked	Average	σ	Average	σ	Average	σ	Average	σ	Average	σ
SS-53A	1.656	1.754	1.829	3810	347	2630	239	1.74	0.08	1.20	0.06	106	2
SS-55	1.636	1.740	1.757	3570	289	2460	199	1.95	0.09	1.34	0.06	98	2
SS-56	1.623	1.726	1.720	3160	428	2180	294	1.80	0.09	1.24	0.06	83	5
SS-57	1.607	1.698	1.679	2660	126	1830	87	1.64	0.14	1.13	0.10	65	13

---

* Average of measurements made for two 5" (12.7 cm) diameter plugs.

** Average of four tests conducted using 4.5" x 1.0" x 0.5" (11.4 cm x 2.5 cm x 1.3 cm) samples. Flexural samples broken on a 3.0" (7.6 cm) span per ASTM procedure C651-70.

*** R_s Scale = 1/2" (1.3 cm) diameter ball and 100 Kg. maj. load. Two measurements made on each of the four samples.

c) Remove material from blender, pass through a fine mesh screen to break up any remaining lumps of boron carbide, and reblend for 1/2 hour.

d) Warm mold (100° C) blended material by using a hydraulic press.

e) Pack green compacts with coke in a sagger, place a layer of charcoal on top of the pack, and bake green compacts to 1000° C according to the same slow schedule specified for the nonadditive subsystems.

f) Using graphite particles as the packing medium, fire the 1000° C baked compacts to 2200° C in an induction furnace employing the following schedule: room temperature to 900° C at 400° C per hour, 900° C to 1600° C at 200° C per hour, 1600° C to 2200° C at 300° C per hour, and hold 1 hour at 2200° C. (A final temperature of 2200° C was used to prevent the melting of the boron carbide.)

The mechanical properties of the boronated materials manufactured from subsystems SS-55 through SS-57 are also displayed in Table VII. Increasing the boron carbide content degraded mechanical properties. The poorer-than-expected mechanical properties of the boronated materials were initially thought to be the result of agglomeration of the boron carbide particles. However, photomicrographs prepared by NASA-Lewis showed that the boron carbide particles were well distributed through the materials. The use of the fine-milled boron carbide, the intensive blending process, and the low final temperature (2200° C) eliminated the agglomeration problem which had been encountered during Task I(5) when boron carbide was used in the manufacture of material system MS-3. The poorer-than-expected mechanical properties may have resulted from some diffusion of the boron from the compacts during baking and/or poor bonding of the boron carbide particles to the base matrix.

3. Modified Boronated Material Subsystems

After analyzing the boronated materials of subsystems SS-55 through SS-57, we concluded that their mechanical properties could be improved if they were pitch impregnated and/or the binder level of the nonboronated base material was increased. Both of these techniques would provide additional pitch binder which could help bond the boron carbide particles to the base matrix. Incorporating boron carbide as a part of the packing medium during final baking also could help to improve the mechanical properties of the boronated materials by preventing the diffusion of the boron. With these ideas in mind, we made tentative plans for the pitch impregnation of 1000° C baked compacts of subsystems SS-55 and SS-56 and the preparation of boronated compacts from a higher binder level material, to be identified as subsystem SS-65.

Subsystem SS-65 had the same composition as that of subsystem SS-55 (Table VII) except the binder level was increased from 70 to 80 pph. The SS-54 mix (Table V) rather than the SS-53 mix was used as the base material for the manufacture of the SS-65 compacts. Except for two minor changes, the same processing procedure used to manufacture the boronated materials from subsystems SS-55 through SS-57 was employed to manufacture the SS-65 material. The two minor processing changes consisted of passing the fine-milled boron carbide through a 325 mesh standard Tyler screen prior to blending it with the SS-54 base mix and using a hammer mill in place of a fine mesh screen to break up any lumps of boron carbide remaining after blending. Apparently, the 80 pph binder level was too high, since all the SS-65 compacts cracked and/or laminated during baking to 1000° C.

Although increasing the binder level of the base material had proven to be an unsuccessful method for improving the mechanical properties of the boronated materials, incorporation of pitch impregnation into their processing yielded significant improvements. Two 1000° C-baked compacts from each of the subsystems SS-55 and SS-56, were impregnated with pitch. The compacts were rebaked to 1000° C and final baked to 2200° C in an induction furnace by using the baking schedule listed in Section IV-B-2 of the report.

To prevent diffusion of the boron during induction baking, we packed the compacts in a sealed graphite capsule, using a mixture of 10 percent boron carbide and 90 percent fine coke as the packing medium. The 2200° C baked pitch-impregnated materials, which were identified as SS-55P and SS-56P, were in very good condition after final baking. The letter "P" following the subsystem number was used to denote pitch impregnation. One compact each of the SS-55P and SS-56P materials subsequently were repacked in the induction furnace by using the diffusion preventative packing procedure and were final baked to 2800° C. A fast 600° C per hour rate of rise between 2200° C and 2800° C along with a short 5-minute hold at 2800° C were used in a further attempt to prevent the diffusion of the boron from the compacts during baking. The 2800° C baked compacts of subsystems SS-55P and SS-56P were assigned the designation SS-66P and SS-67P, respectively. A complete description of subsystems SS-55P, SS-56P, SS-66P, and SS-67P is presented in Table VIII.

Table IX presents a comparison of the mechanical properties of the boronated materials manufactured from subsystems SS-55, SS-55P, SS-56, SS-56P, SS-66P, and SS-67P. Incorporating pitch impregnation in the processing of the SS-55P and SS-56P materials along with the use of the diffusion preventative packing medium during final baking resulted in their mechanical properties being significantly better than those of their non-pitch-impregnated counterparts. Weight increases of approximately 4. 5 percent were measured for the SS-55P and SS-56P compacts following pitch impregnation and rebaking to 1000° C. Increasing the final baking temperature of the material containing 5 pbw boron carbide to 2800° C (SS-66P) yielded only minor changes in mechanical properties. However, increasing the final baking temperature of the material containing 7. 5 pbw boron carbide to 2800° C yielded a lower density material (SS-67P) which was very soft and weak. Increases in both the total open porosity and the degree of crystallinity probably accounted for the poorer mechanical properties of the SS-67P material. These effects will be discussed further in later sections of the report.

TABLE VIII

Identification of Pitch-Impregnated Subsystems SS-55P, SS-56P, SS-66P and SS-67P

Subsystem No.	Base Material		Final Baking Temperature	Additive	Impregnant
	Particulate Solid Raw Material	Binder Raw Material			
SS-53A	Fine Milled CHP Artificial Graphite (80pbw) & Thermax (20 pbw)	No. 30 Medium Pitch (70 pph)	2800° C	----	----
SS-55	SS-53A Base Material (100pbw)		2200° C	B_4C (5 pbw)	----
SS-56	SS-53A Base Material (100pbw)		2200° C	B_4C (7. 5 pbw)	----
SS-55P	SS-53A Base Material (100pbw)		2200° C	B_4C (5 pbw)	1000° C baked Compacts Impregnated with Pitch and Rebaked to 1000° C Prior to Final Baking to 2200° C
SS-56P	SS-53A Base Material (100pbw)		2200° C	B_4C (7. 5 pbw)	1000° C Baked Compacts Impregnated with Pitch and Rebaked to 1000° C Prior to Final Baking to 2200° C
SS-66P	SS-53A Base Material (100pbw)		2800° C	B_4C (5 pbw)	1000° C Baked Compacts Impregnated with Pitch and Rebaked to 1000° C Prior to Final Baking to 2800° C
SS-67P	SS-53A Base Material (100pbw)		2800° C	B_4C (7. 5 pbw)	1000° C Baked Compacts Impregnated with Pitch and Rebaked to 1000° C Prior to Final Baking to 2800° C

Note: Proportions are parts by weight (pbw).

Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials (pph).

Boron carbide addition blended with SS-53A base mix just prior to molding "green" compacts.

The "green" compacts of the above materials were all molded at a pressure of 5000 psi and a temperature of 100° C.

TABLE IX

Material Properties of Pitch-Impregnated Subsystems

	Materials					
	SS-55	SS-55P	SS-66P	SS-56	SS-56P	SS-67P
	B_4C (5 pbw)	B_4C (5 pbw)	B_4C (5 pbw)	B_4C (7.5 pbw)	B_4C (7.5 pbw)	B_4C (7.5 pbw)
	No Impregnant	Pitch Impregnated	Pitch Impregnated	No Impregnant	Pitch Impregnated	Pitch Impregnated
Material Properties	2200° C	2200° C	2800° C	2200° C	2200° C	2800° C
Final Baked Bulk Density (g/cc)*						
Maximum	1.768	1.857	-----	1.731	1.852	-----
Minimum	1.745	1.853	-----	1.708	1.848	-----
Average	1.757	1.855	1.837	1.720	1.850	1.792
n	2	2	1	2	2	1
Flexural Strength**						
(in units of psi)						
Maximum	3930	6160	6600	3630	6200	4350
Minimum	3290	4970	6260	2600	5780	4190
Average	3570	5560	6430	3160	5990	4270
n	4	2	2	4	2	2
(in units of N/cm^2)						
Maximum	2710	4240	4550	2500	4270	3000
Minimum	2270	3420	4310	1790	3980	2890
Average	2460	3830	4430	2180	4130	2940
n	4	2	2	4	2	2
Elastic Modulus**						
(in units of 10^6 psi)						
Maximum	2.07	2.46	2.60	1.89	2.65	2.54
Minimum	1.84	2.42	2.55	1.71	2.48	2.45
Average	1.95	2.44	2.58	1.80	2.57	2.49
n	4	2	2	4	2	2
(in units of 10^6 N/cm^2)						
Maximum	1.43	1.69	1.79	1.30	1.83	1.75
Minimum	1.27	1.67	1.76	1.18	1.71	1.69
Average	1.34	1.68	1.78	1.24	1.77	1.72
n	4	2	2	4	2	2
Rockwell "S" Hardness***						
Maximum	101	115	97	91	113	25
Minimum	96	108	94	75	105	20
Average	98	112	96	83	109	23
n	8	4	4	8	4	4

---

* Measurements made for 5" (12.7 cm) diameter plugs.

** Conducted using 4.5" x 1.0" x 0.5" (11.4 cm x 2.5 cm x 1.3 cm) samples. Flexural samples broken on a 3.0" (7.6 cm) span per ASTM procedure (C651-70).

*** R_s Scale = 1/2" (1.3 cm) diameter ball and 100 Kg. maj. load. Two measurements made on each of the flexural samples.

The materials manufactured from subsystems SS-55P, SS-56P, and SS-66P were the strongest and hardest materials developed under the scope of this Contract. The highest average flexural strength and hardness measurements previously recorded for any of the materials developed under Tasks I through VII(5,6,7) were 4750 psi (3270 N/cm^2) and 88 Rockwell "S". Since high hardness, strength, and modulus are necessary for producing wear and erosion-resistant carbon-graphite seal ring materials, the materials manufactured from subsystems SS-55P, SS-56P, and SS-66P should be better materials for meeting the goal of this Contract than those previously developed. The mechanical properties of these three boronated materials compare more closely with those of commercial seal ring Grade CDJ-83 than do the mechanical properties of any of the other materials developed during this Contract. Grade CDJ-83 has a nominal bulk density of 1.76 g/cc, a flexural strength of 8800 psi (6100 N/cm^2), an elastic modulus of 3.2 x 10^6 psi (2.2 x 10^6 N/cm^2), and a Rockwell "E" hardness of 105. As discussed Topical Report NASA CR-72799,(5) some sacrifice in strength and hardness was necessary during the development of the oxidation-resistant, carbon-graphite materials.

SECTION V

MATERIAL PROPERTIES

(TASK IX)

A. Property Requirements of Seal Ring Carbon-Graphite Materials

The goal of this Contract is the development of a carbon-graphite material for use as a self-acting seal in advanced gas turbine engines. High oxidation resistance is a primary requirement of the material if it is to withstand the high operating temperatures. Since self-acting seals experience relatively high-speed sliding contact during limited periods of operation, good wear resistance is also a requirement. High hardness, strength, and modulus, together with the proper impregnants and mating materials, are necessary attributes for wear-resistant carbon-graphite seal ring materials. High hardness also is required to ensure the erosion resistance of the material. Erosion resistance is an important requirement for a self-acting seal material, since debris passing through the gas film formed between the self-acting seal and the seat during engine operation tends to score and erode the primary ring. A carbon-graphite material used as a self-acting seal must also have a high thermal conductivity to provide rapid transfer of the deleterious frictional heat which can develop during periods of sliding contact. Dimensional stability is a desirable property of a seal ring material, although thermal expansion is not critical for this application, since the carbon will be controlled by an outer shrink ring during operation.

Aside from the material properties that are essential for good performance, a seal ring material should also be readily machinable, since seal dam widths as small as 0.020-inch (0.05 cm) often are present in seal design. The compacts manufactured during the Task VIII screening study were all found to be more easily machinable than commercial seal ring Grade CDJ. The good machinability of the carbon-graphite articles manufactured during Task VIII resulted from the use of a large proportion of particulate graphite in the filler systems and a final heat treatment temperature ranging between 2200° C and 2800° C. Due to the abrasiveness of the boron carbide particles, some of the boronated materials manufactured during Task VIII were, however, not so machinable as the carbon-graphite materials manufactured during Tasks III(6) and VI(7).

Under the scope of Task IX, the following material properties were measured for selected carbon-graphite seal ring bodies manufactured during Task VIII:

1. Mechanical Properties
    - a) Density before and after impregnation with an oxidation-inhibiting treatment.
    - b) Flexural strength
    - c) Elastic modulus
    - d) Hardness
2. Oxidation Resistance, Porosity, and Structure
    - a) Oxidation resistance compared with that of a carbon-graphite seal material currently in use.
    - b) Total open porosity
    - c) Examination of the carbon-graphite materials by photomicrographs.

Except for the measurement of the density after impregnation with an oxidation-inhibiting treatment, the mechanical properties were measured during Task VIII for all the materials. The mechanical properties had been used as the basis for screening the materials. The materials prepared from subsystems SS-53A, SS-55P, SS-56P, SS-66P, and SS-67P were selected as warranting further material characterization, since results of the mechanical property (Section IV-B-3) tests show that at least three of the selected five materials should be better-performing and more erosion-resistant carbon-graphite materials than those previously developed. This section of the report is divided into subsections with the next subsection discussing the total open porosities of the five selected materials. The remaining subsections cover the examination of the materials by photomicrographs and the oxidation studies.

B. Total Open Porosity

Carbon-graphite seal ring bodies must be low porosity materials so that they will be impervious to the fluids which they seal. As demonstrated during the experimental portion of Task I,(5) the mechanical properties and oxidation resistance of a carbon-graphite compact are greatly affected by the choice of raw materials, composition, and final baking temperature used for its manufacture. Although the degree of crystallinity of a carbon-graphite body greatly affects its material properties, the porosity of the compact also has some effect. Reducing the porosity of a formed article should result in an improvement in the mechanical and chemical properties. Decreasing the porosity of a compact reduces the number of interconnected voids, and the remaining isolated voids are less damaging to the mechanical properties. Reducing the porosity of a carbon-graphite compact also should increase its oxidation resistance.

The carbonization of a resin impregnant was found during Tasks III through VII(6, 7) to be a good way to reduce the porosity of a carbon-graphite compact. Resin impregnation has been found to be better than conventional pitch impregnation for reducing the permeability of a carbon-graphite material, since the lower viscosities and increased wetting of the resins allow them to block pores as well as larger open volumes. Pitch impregnation can, however, have the effect of increasing strength and density without markedly reducing permeability, due to the tendency of pitch to coke out only in the voids of large effective pore radius.(8) The possibility of effecting large improvements in the strengths of the materials developed under this Contract was the reason for investigating pitch impregnation during Task VIII.

Table X presents the percent total porosities of the compacts of formulations Nos. 1 and 1X and subsystems SS-53A, SS-55P, SS-56P, SS-66P, and SS-67P. The values presented for the materials manufactured from formulations Nos. 1 and 1X (compositions listed in Table I) were determined during Task IV,(6) but have been included for comparison. Table X also displays the percent total porosity for commercial seal ring Grade CDJ. These values were calculated by using the following equation:

$$\text{Percent Total Porosity} = 100\text{X}\,\frac{\text{Helium Density} - \text{Bulk Density}}{\text{Helium Density}}.$$

TABLE X

Percent Total Open Porosities

Material	Helium Density (g/cc)	Bulk Density (g/cc)	Percent Total Open Porosity	Average Mechanical Properties		
				Flexural Strength (in units of N/cm²)	Elastic Modulus (in units of 10^6 N/cm²)	Rockwell "S" Hardness
Formulation No. 1*	2.05	1.71	16.6	2630	0.90	80
Formulation No. 1X*	1.94	1.73	10.8	3090	1.01	85
Subsystem SS-53A	2.06	1.82	11.7	2630	1.20	106
Subsystem SS-55P	2.04	1.85	9.3	3830	1.68	112
Subsystem SS-56P	2.05	1.85	9.8	4130	1.77	109
Subsystem SS-66P	2.04	1.84	9.8	4430	1.78	96
Subsystem SS-67P	2.04	1.79	12.3	2940	1.72	23
Grade CDJ	1.84	1.76	4.6	6100	2.20	--

* Results determined during Task IV, but presented here for purposes of comparison.

$$\text{Percent total porosity} = 100\text{X}\ \frac{\text{Helium Density - Bulk Density}}{\text{Helium Density}}$$

The value obtained by using this equation is the ratio of the total open pore volume to the volume occupied by the pores and the carbonaceous material in the compact.

Subsystem SS-53A was a modification of formulation No. 1 designed to yield a carbon-graphite material with improved mechanical properties. The two materials differed in that subsystem SS-53A specified a fine milled particulate graphite filler, an increased pitch binder level (70 pph versus 60 pph), intensive mixing, and the warm molding of green compacts. The results presented in Table X show that these modifications resulted in the total open porosity of the SS-53A material being noticeably lower than that of the formulation No. 1 material. Due to the reduction in porosity, improvements in the bulk density, modulus, and hardness of the SS-53A material were obtained. The lack of improvement in the flexural strength of the SS-53A material as compared with that of the formulation No. 1 material may indicate that the binder did not adequately "wet" the filler material.

No definite conclusion as to which type of impregnant is best can be drawn from the comparison of the pitch impregnated Task VIII materials with the resin impregnated materials manufactured during Tasks III and VI. (6, 7) Too many variables, other than the type of impregnant used, exist between the Task VIII materials and those manufactured during Tasks III and VI. (6, 7) The finer particle size of the CHP graphite, the use of boron carbide as an oxidation inhibiting additive, and the adjustment of the final baking temperature of the Task VIII materials all affected their final properties. However, the data presented in Table X do show that the pitch impregnated materials of subsystems SS-55P, SS-56P, and SS-66P possess significantly better material properties than those of the resin-impregnated formulation No. 1X material, whereas the percent total open porosity of the four materials are almost the same. This observation lends support to the theory that pitch-impregnation can significantly improve the mechanical properties of a carbon-graphite material without greatly reducing the permeability of the material.

The total open porosities of the boronated materials of subsystems SS-55P, SS-56P, SS-66P, and SS-67P help to explain the changes in mechanical properties resulting from the increase in the final baking temperature of the latter two materials. Increasing the final baking temperature resulted in the expansion of the compacts so that the volumes of the 2800° C baked SS-66P and SS-67P compacts were larger than those of their 2200° C baked counterparts. The expansion of the compacts may have resulted from the particulate graphite in the compacts being doped substitutionally with boron. The Task I(5) literature search had pointed out that graphite can be doped substitutionally with boron in amounts up to a B/C atom ratio of at least 10^{-2} by heating graphite-boron powders to greater than 2500° C.(9) The vapor pressure of the boron also could be responsible for the expansion or "puffing" of the structures of the compacts baked to 2800° C. Due to the expansion of the compacts upon baking to 2800° C, the total open porosities of the SS-66P and SS-67P compacts were 0. 5 and 2. 5 percent greater than those of their 2200° C baked counterparts. The 0. 5 percent increase in total open porosity probably accounts for the 2800° C baked SS-66P material being a little less dense and slightly softer than the 2200° C baked SS-55P material. The larger 2. 5 percent increase in the total open porosity of the 2800° C baked SS-67P material accounts in part for its mechanical properties being considerably poorer than those of the 2200° C baked SS-56P material. A considerable increase in the degree of crystallinity of the SS-67P material as compared with that of the SS-56P material also probably had a large effect on degrading the mechanical properties of the former material. The increase in the degree of crystallinity of the SS-67P material will be discussed further in a later section.

The internal structures of the carbon-graphite seal ring bodies manufactured from subsystems SS-53A, SS-55P, SS-56P, and SS-66P appeared by visual examination to be very homogeneous and fine grained. No large pores or voids were noted in the compacts examined. A measure of the uniformity of the structures is obtained by examining the percent increases in weight of the compacts after impregnation with the No. 121 oxidation-inhibiting treatment. The uniformity of impregnation reflects the uniformity of the internal structure of the impregnated material. Table XI lists the treat pickups measured for the 1/2-inch (1. 3 cm) cubes of subsystems SS-53A, SS-55P, SS-56P, SS-66P, and SS-67P after impregnation with the No. 121 oxidation-inhibiting treatment.

TABLE XI

Weight Pickups and Densities for Materials Impregnated with No. 121 Oxidation-Inhibiting Treatment

	SS-53A-121	SS-55P-121	SS-56P-121	SS-66P-121	SS-67P-121
Weight Percent Treat Pickup*					
Maximum	1.41	0.97	0.98	1.37	1.98
Minimum	1.28	0.86	0.85	0.98	1.66
Average	1.34	0.92	0.88	1.10	1.78
Standard Deviation	0.06	0.04	0.05	0.15	0.12
V**	4.8	4.1	5.8	13.6	7.0
n***	6	6	6	6	6
Bulk Density Before Impregnation With No. 121 Oxidation-Inhibiting Treatment					
Maximum	1.821	1.872	1.877	1.858	1.807
Minimum	1.798	1.854	1.861	1.830	1.772
Average	1.810	1.866	1.872	1.847	1.790
Standard Deviation	0.020	0.010	<0.001	0.020	0.017
n	6	6	6	6	6
Bulk Density After Impregnation With No. 121 Oxidation-Inhibiting Treatment					
Maximum	1.844	1.889	1.907	1.884	1.838
Minimum	1.825	1.872	1.880	1.849	1.801
Average	1.837	1.883	1.893	1.867	1.822
Standard Deviation	<0.001	<0.001	0.017	0.020	0.017
n	6	6	6	6	6

---

* Weight percent treat pickup $= 100 \times \left(\frac{\text{Weight of Sample after Treatment - Original Weight of Sample}}{\text{Original Weight of Sample}} \right)$

** V = Coefficient of Variation = $100 \times \sigma/\text{average}$

*** The number of 1/2" (1.3 cm) cubes (oxidation testing samples) impregnated with the No. 121 treatment.

The materials impregnated with the oxidation-inhibiting treatment were identified (Table XI) by the formulation number followed by the number 121 (e. g., subsystem SS-53A-121). Comparison of the treat pickups listed in Table XI to the corresponding total open porosities displayed in Table X shows the expected general trend of increasing treat pickup with increasing porosity. Table XI displays the coefficient of variation for the treat pickups ("V" in Table XI). The coefficients of variation indicate that the uniformity of the materials manufactured from Subsystems SS-53A-121, SS-55P-121, and SS-56P-121 is better than that of the formulation No. 1X-121 (composition listed in Table I) which was manufactured during Task III.(6) The formulation No. 1X-121 material had an average No. 121 treat pickup of 1. 59 percent with a coefficient of variation of 6. 2. The uniformity of the subsystem SS-66P-121 material appears to be poor, since its coefficient of variation was one of the highest of the materials developed for this Contract.

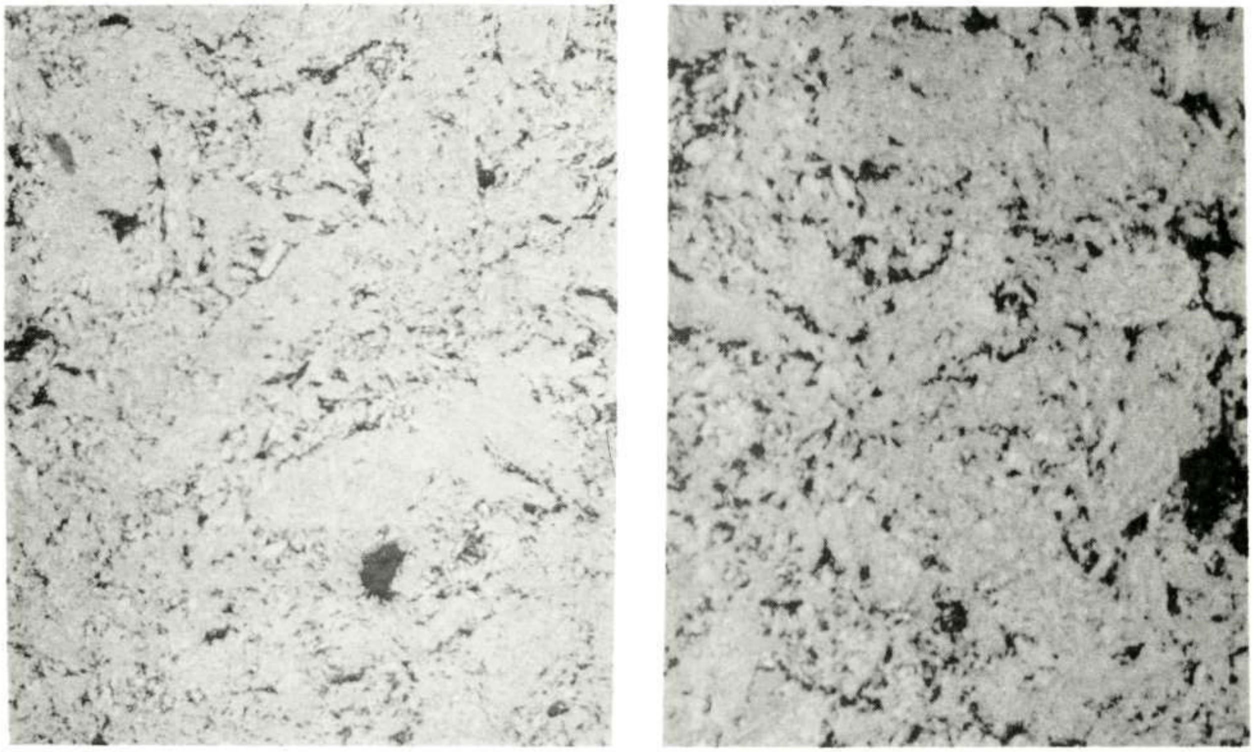
Impregnation of the selected five materials (Table XI) with the No. 121 oxidation-inhibiting treatment resulted in an increase in their respective bulk densities. The impregnation with the No. 121 treatment probably had little effect on the strengths and hardnesses of the materials, since the pickups are relatively low and since no additional carbonaceous material was added to the compacts as in the case when a pitch or resin impregnant is carbonized. The bulk densities listed in Table XI were measured for the treated 1/2-inch (1. 3 cm) cubes which were later used for the oxidation testing of the five materials.

The percent total open porosities for the seal ring bodies of subsystems SS-53A, SS-55P, SS-56P, SS-66P, and SS-67P indicate that all five materials are potentially good carbon-graphite seal ring materials. All five of the subsystems resulted in fine-grain materials with relatively low porosity. Of the five materials, those manufactured from subsystems SS-55P and SS-56P appear to be the best, since they have the lowest total open porosities and most uniform structure.

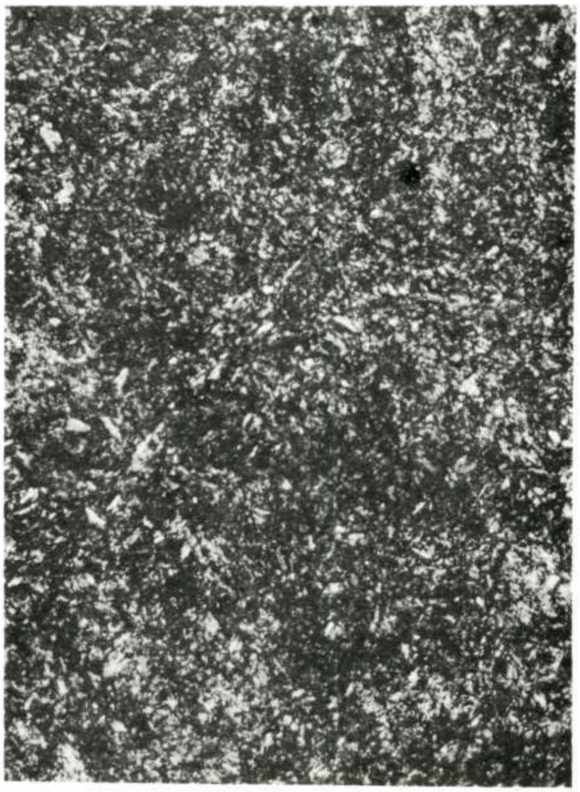
C. Photomicrographs

Photomicrography is a good technique for examining the structure and composition of a carbon-graphite material. Figures 1 through 5 are photomicrographs of the subsystems SS-53A, SS-55P, SS-56P, SS-66P, and SS-67P materials. Each figure consists of three photomicrographs: two taken at magnifications of 250X and 500X with bright field illumination and a third taken at a magnification of 250X with polarized light. The photomicrographs taken with bright field illumination show the uniformity and structure of the materials. The photomicrographs taken with polarized light give a measure of the degree of crystallinity of the materials. When these photomicrographs were prepared, the positioning of the samples under the microscope was controlled so that the photographs are true representations of the structures being examined.

The photomicrographs prepared with bright field illumination show that subsystems SS-53A, SS-55P, SS-56P, SS-66P, and SS-67P are fine-grain materials. Subsystems SS-53A, SS-55P, and SS-56P materials have uniform distributions of interconnected voids which appear as dark areas in the photographs. These interconnected voids would allow for easy passage of the No. 121 treatment through the structures of the three materials which would account for their low coefficients of variation of percent treat pickup ("V" in Table X). Subsystems SS-66P and SS-67P yielded materials which appear in the photomicrographs to have rather localized areas of voids that are not greatly interconnected. This observation is particularly true for the SS-66P materials. The localized areas of voids and the lack of interconnection between them probably account for the higher coefficients of variation of percent treat pickup previously reported for the SS-66P and SS-67P materials. The formation of "catalytic graphite" during final baking to 2800° C probably accounts for the rather nonuniform internal structures of the SS-66P and SS-67P materials. Recrystallization of the graphite may have partially blocked the existing open porosity of the compacts, resulting in the formation of new holes in the stock.

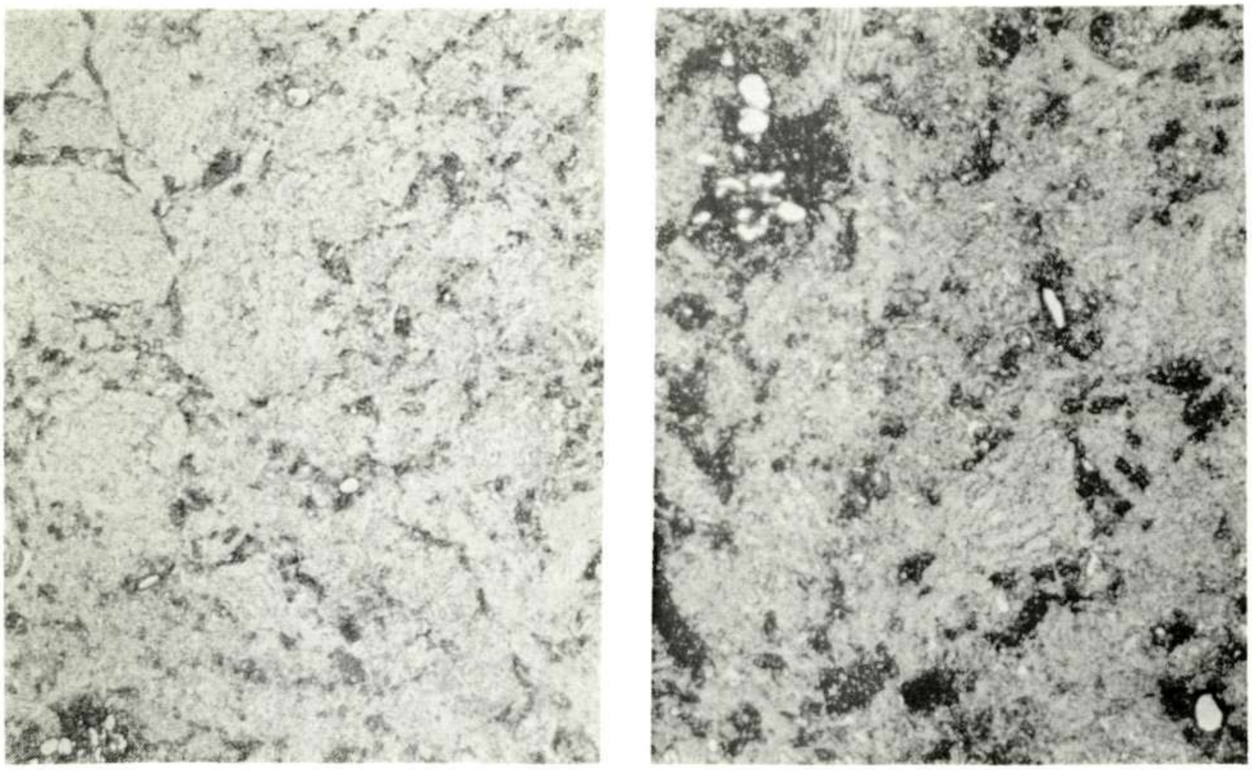


250X (22081101-1-01) 500X (22081101-1-02)

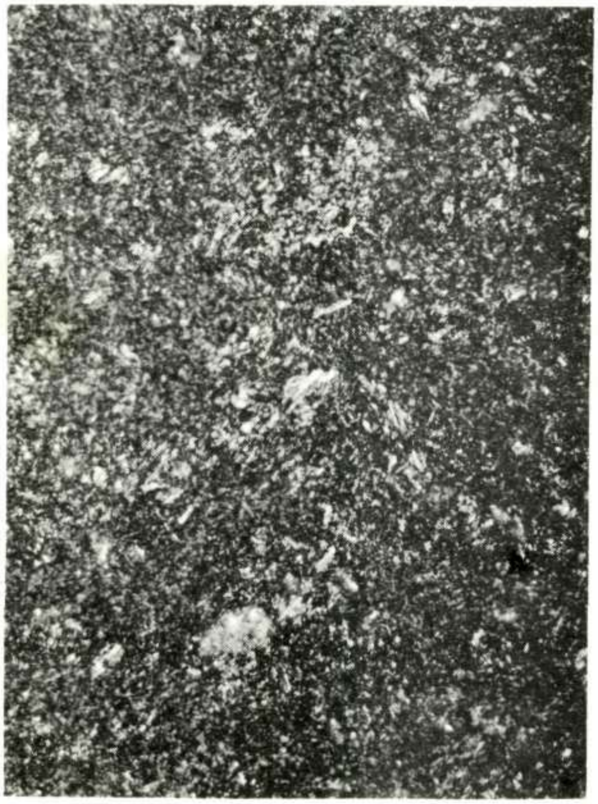


250X - Polarized Light

Figure 1. Photomicrographs of Subsystem SS-53A Material.

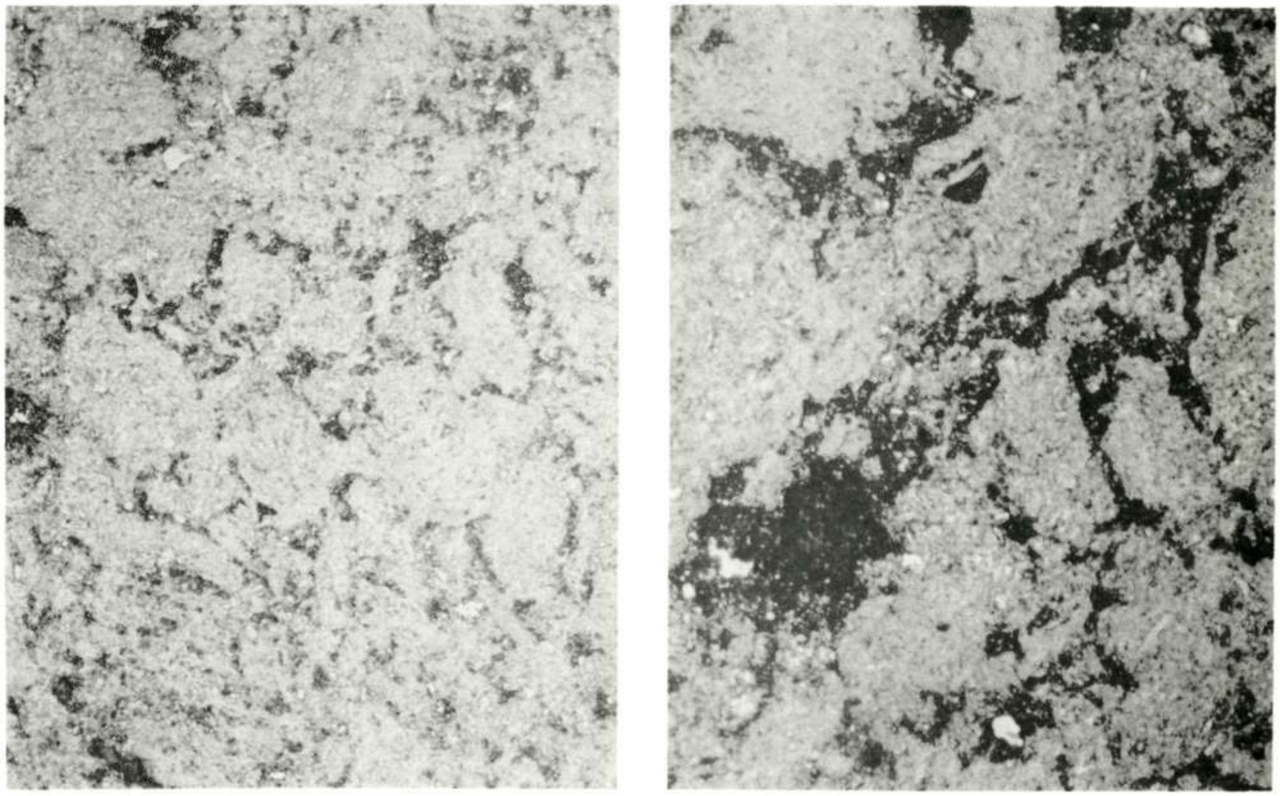


250X (22081101-2-01) 500X (22081101-2-02)

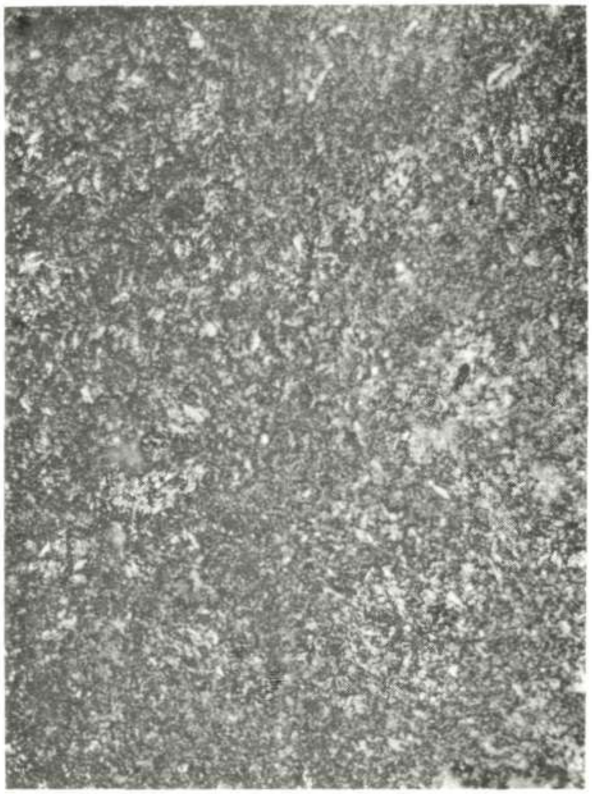


250X - Polarized Light

Figure 2. Photomicrographs of Subsystem SS-55P Material.

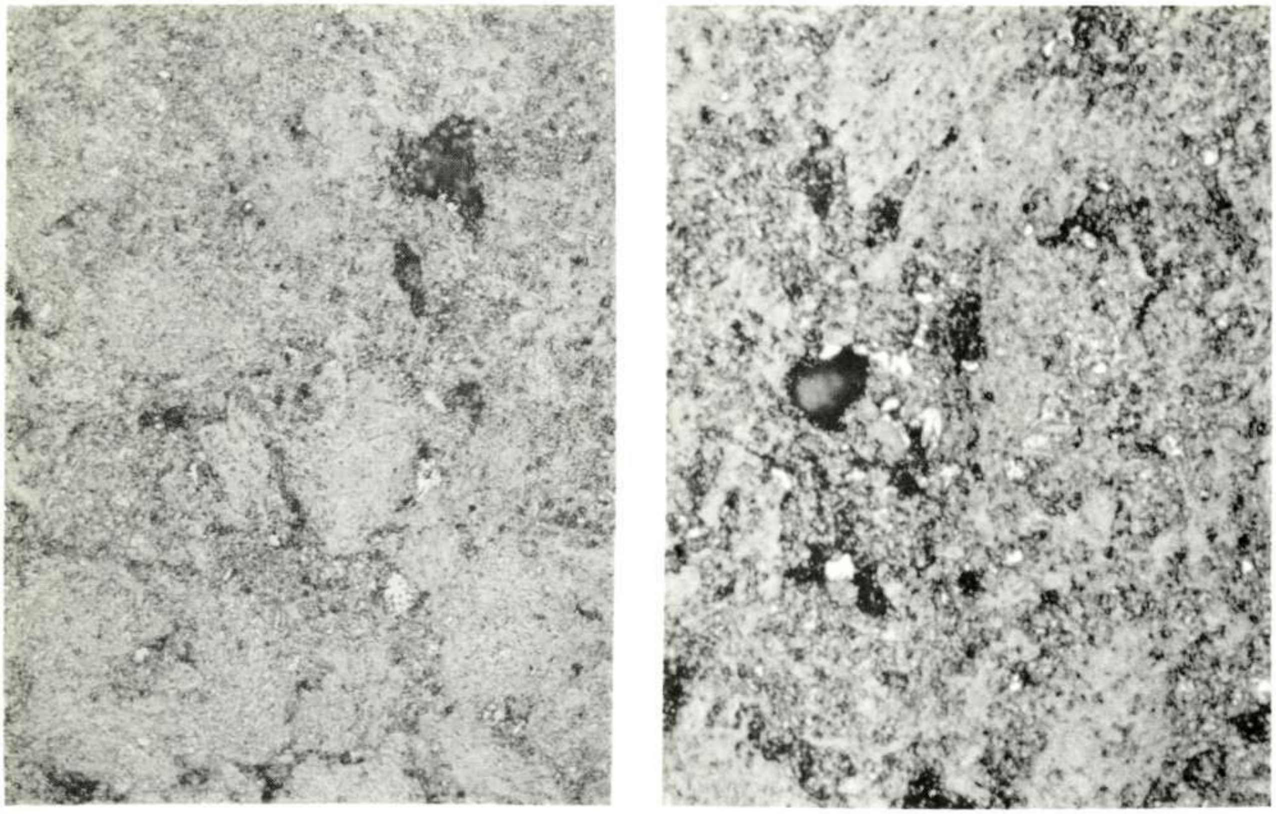


250X (22081101-3-01) 500X (22081101-3-02)

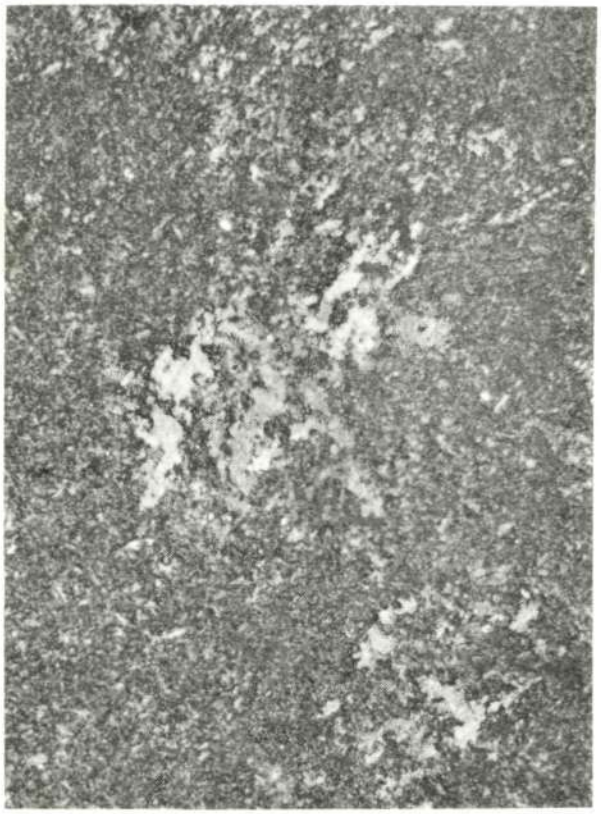


250X - Polarized Light

Figure 3. Photomicrographs of Subsystem SS-56P Material.

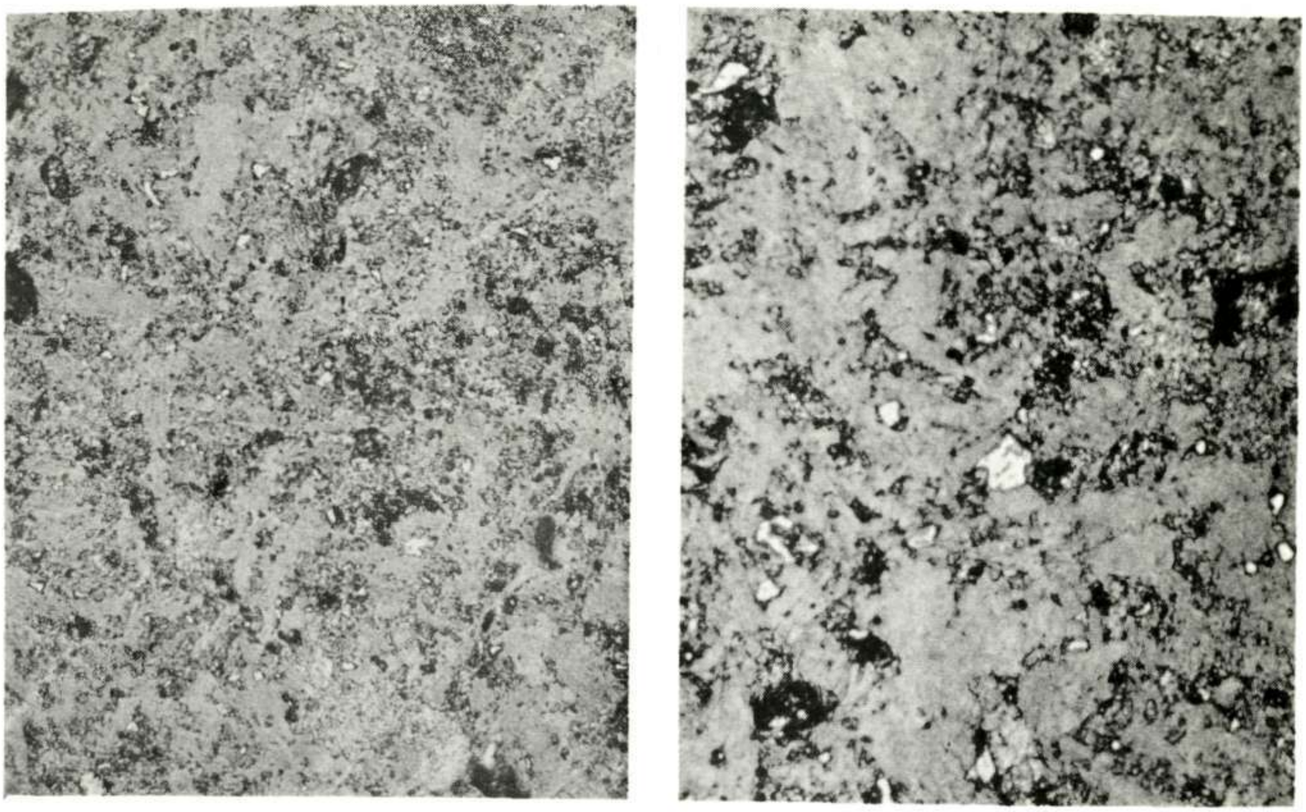


250X (22081101-4-01) 500X (22081101-4-02)

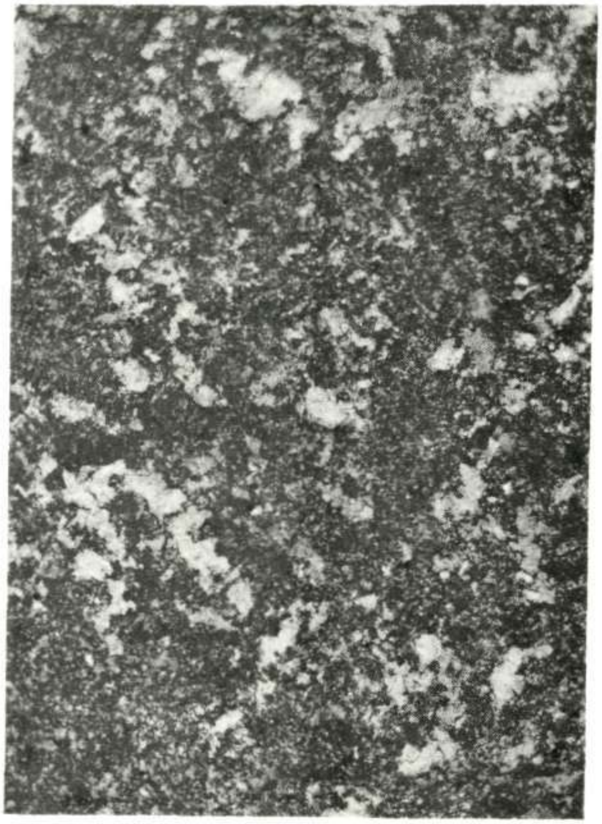


250X - Polarized Light

Figure 4. Photomicrographs of Subsystem SS-66P Material.



250X (22081101-5-01) 500X (22081101-5-02)



250X - Polarized Light

Figure 5. Photomicrographs of Subsystem SS-67P Material.

The photomicrographs prepared with bright field illumination show the fine milled boron carbide particles in the structures of the boronated materials. The boron carbide particles appear as very bright spots in the photomicrographs of the four boronated materials, especially in the photos taken at 500X. These bright spots probably are agglomerates of the very small boron carbide particles, but they still indicate that the boron carbide additive is fairly well distributed through the structures of the boronated materials. The intensive blending process discussed previously in Section IV-B-2 and the use of very fine boron carbide thus were good approaches for obtaining a uniform dispersion of the boron carbide. Comparison of the photomicrographs of the SS-66P and SS-67P materials with those of the corresponding SS-55P and SS-56P materials show that little or no boron carbide was lost by diffusion as a result of increasing the final baking temperature from 2200° C to 2800° C. This observation was confirmed by the boron contents determined analytically for the four materials. The boron contents are listed in Table XII. Diffusion of the boron carbide during induction baking was prevented by packing the compacts in a sealed graphite capsule with a packing medium containing 10 weight percent boron carbide.

TABLE XII

Boron Contents of Boronated Materials

Material	Boron Carbide Addition (parts by weight)	Final Baking Temperature (° C)	Boron Content (Wt. %) Green* Compacts	Boron Content (Wt. %) Final Baked** Compacts
SS-55P	5	2200	3. 8	3. 8
SS-66P	5	2800	3. 8	3. 8
SS-56P	7. 5	2200	5. 6	5. 3
SS-67P	7. 5	2800	5. 6	5. 3

---

* Calculated using following equation in which 80% (by weight) of the boron carbide (B_4C) is boron (B).

$$\%B = 80 \times \left(\frac{\text{wt. of } B_4C}{\text{wt. of SS-53A base mix + wt. of } B_4C}\right)$$

** Determined Analytically

The photomicrographs taken using polarized light for illumination give an indication of the degree of crystallinity of the five materials. The beneficial value of using polarized light for illumination results from the fact that graphite is a birefringent material due to its anisotropy. When a carefully polished sample of a carbon-graphite material is slowly rotated while being illuminated with polarized light, a point is reached at which the birefringent property of the graphite crystals causes them to be visually discernible from the background carbon material. The background carbon material is not birefringent because it is relatively isotropic, and, thus, its appearance under polarized light remains constant as the sample is rotated 360°. Due to the birefringent property of the graphite crystals, they will seem to repeatedly appear and disappear relative to the background carbon material as the sample is rotated 360°.

The photomicrographs prepared by using polarized light (Figures 1 through 5) visually prove that boron carbide acts as a graphitization catalyst when added to a carbon-graphite material. Comparison of the polarized light photomicrographs in Figures 1 through 3 show that all three materials look alike. The boron carbide additions to the 2200° C baked SS-55P and SS-56P materials resulted in the two materials having degrees of crystallinity very similar to that of the 2800° C baked nonboronated SS-53A material. The polarized light photomicrographs of the SS-66P and SS-67P materials (Figures 4 and 5) actually picture the graphite crystal growth resulting from the addition of the boron carbide. This recrystallized graphite appears as light areas in the polarized light photomicrographs of the two materials. The SS-66P and SS-67P materials are more crystalline than the SS-53A, SS-55P, and SS-56P materials, with the SS-67P material definitely being the most crystalline of the selected five materials. Its high degree of crystallinity is a major cause of the poor mechanical properties previously reported for the SS-67P material.

The photomicrographs of the SS-53A, SS-55P, SS-56P, SS-66P and SS-67P materials show that they are all fine-grain and generally uniform materials. The five materials thus all appear to be potentially good carbon graphite seal ring materials. Due to their increased degrees of crystallinity, the 2800° C baked SS-66P and SS-67P materials would be expected to be more oxidation-resistant than their corresponding 2200° C baked counterparts.

D. Oxidation Tests

High oxidation resistance is a primary requirement for a carbon-graphite seal ring material which is exposed to ambient air temperatures up to 1300° F (704° C). A material with a high degree of crystallinity is needed, since the crystallinity of a carbon-graphite material greatly affects the rate at which it oxidizes. The compositions formulated under the scope of this Contract were designed to yield carbon-graphite seal ring bodies with high degrees of crystallinity. Further increases in oxidation resistance are obtained by including oxidation-inhibiting additives, such as boron carbide, in the carbon-graphite seal ring materials and by impregnating the seal ring bodies with oxidation-inhibiting treatments, such as the No. 121 treatment. During Task IX, oxidation tests were conducted at 1300° F (704° C) with 1/2-inch (1. 3 cm) cubes prepared from the compacts of subsystems SS-53A, SS-55P, SS-56P, SS-66P, and SS-67P. Commercial seal ring Grade CDJ was used as a standard for the oxidation testing. The 1/2-inch (1. 3 cm) cubes were impregnated with the No. 121 treatment before being exposed to the oxidizing conditions; the No. 121 treat pickups were presented in Table XI.

The oxidation test procedure and equipment employed during Task IX were the same as those used during the oxidation studies of Tasks I, IV, and VII. (10, 11, 12) The samples were placed in one-inch (2. 54 cm)i. d. quartz tubes, which subsequently were supported in a small electrically heated furnace. The quartz tubes were used to keep the samples from contacting the metal support (which might have acted as an oxidation catalyst) and to allow the removal of the oxidation samples from the furnace without damaging them. Figure 6 is a schematic of the oxidation testing apparatus. The furnace has a split door which is propped open during oxidation testing so that a 3/8-inch (0. 95 cm) gap was maintained across the entire face of the furnace between the upper and lower halves of the door. The quartz tubes containing the samples were supported so that the samples were in line with the gap between the two sections of the door. Air passing through the gap in the door also flowed around the samples as shown in Figure 6.

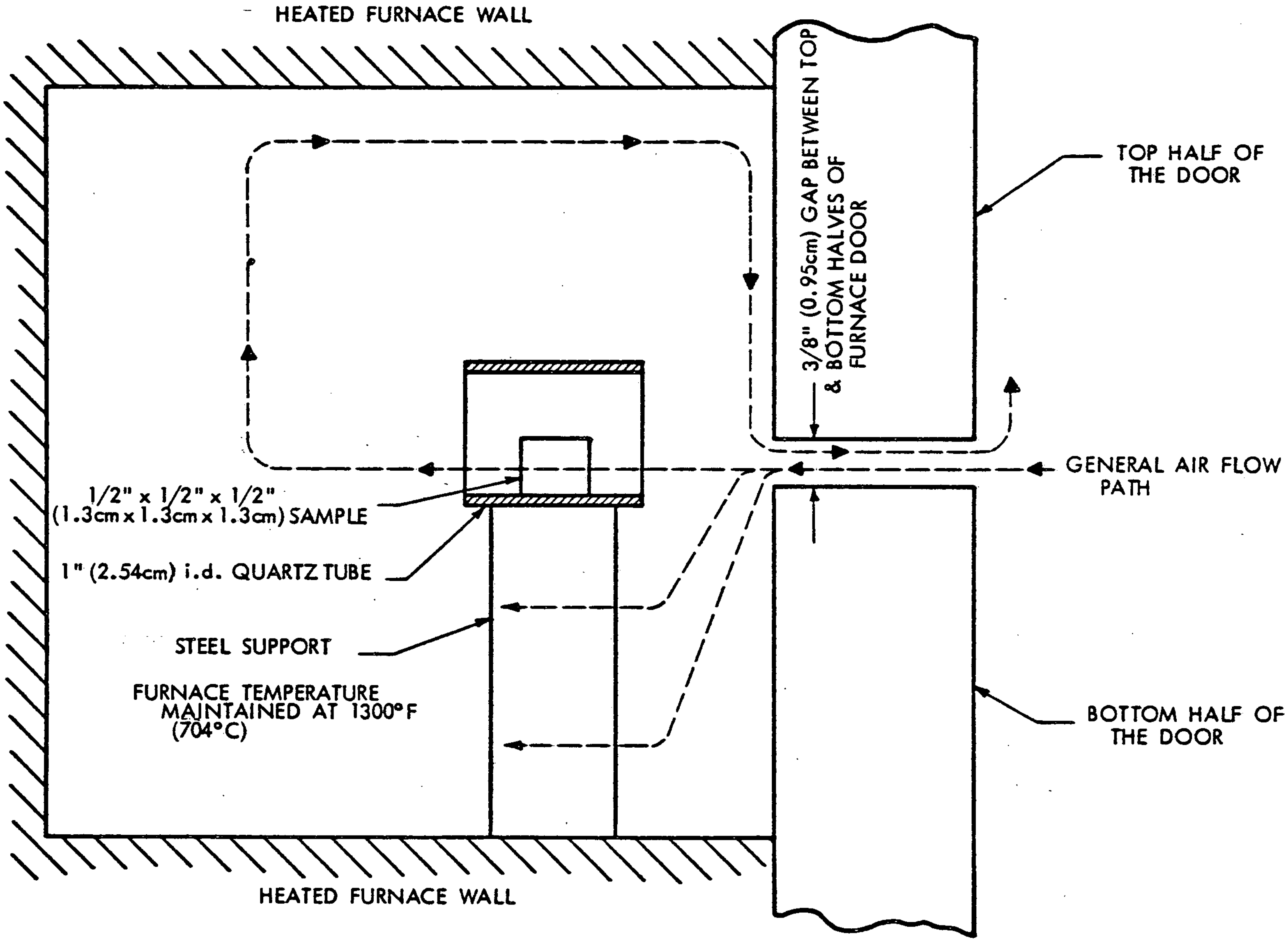


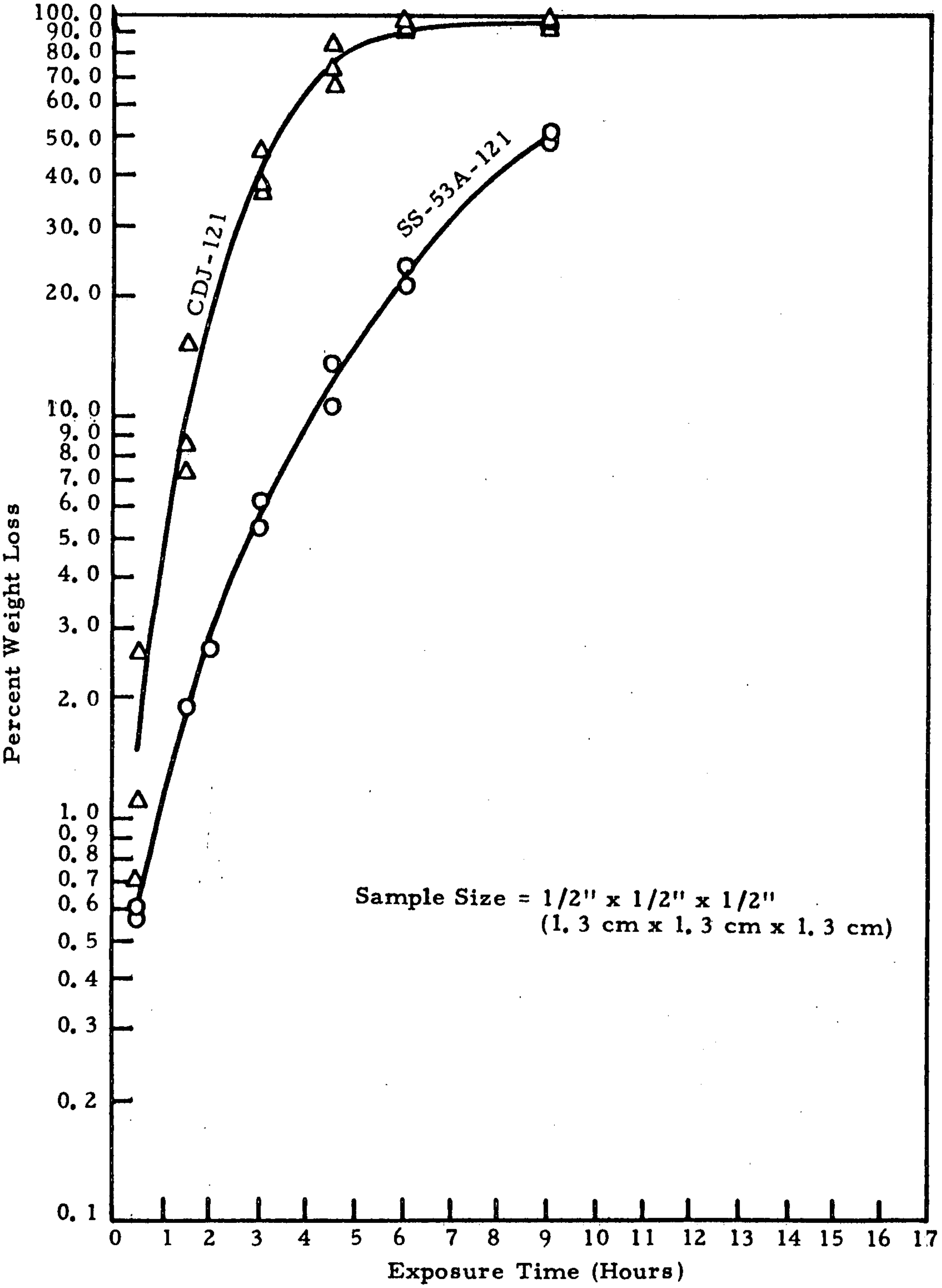
Figure 6. Oxidation Testing Apparatus

N-23865

At the beginning of the test, the samples were weighed and placed into the quartz tubes, after which the tubes containing the samples were weighed and placed inside the 1300°F (704° C) furnace chamber. After 1/2-hour exposure to the oxidizing conditions, the quartz tubes containing the samples were removed from the furnace, cooled to room temperature, weighed, and placed back inside the furnace for another exposure period. This procedure was continued until the samples had been exposed to the oxidizing conditions for a minimum of nine hours with incremental weight losses being measured at specified times. A preliminary test had shown that the weight of the empty quartz tubes remained constant when exposed to the 1300° F (704° C) air.

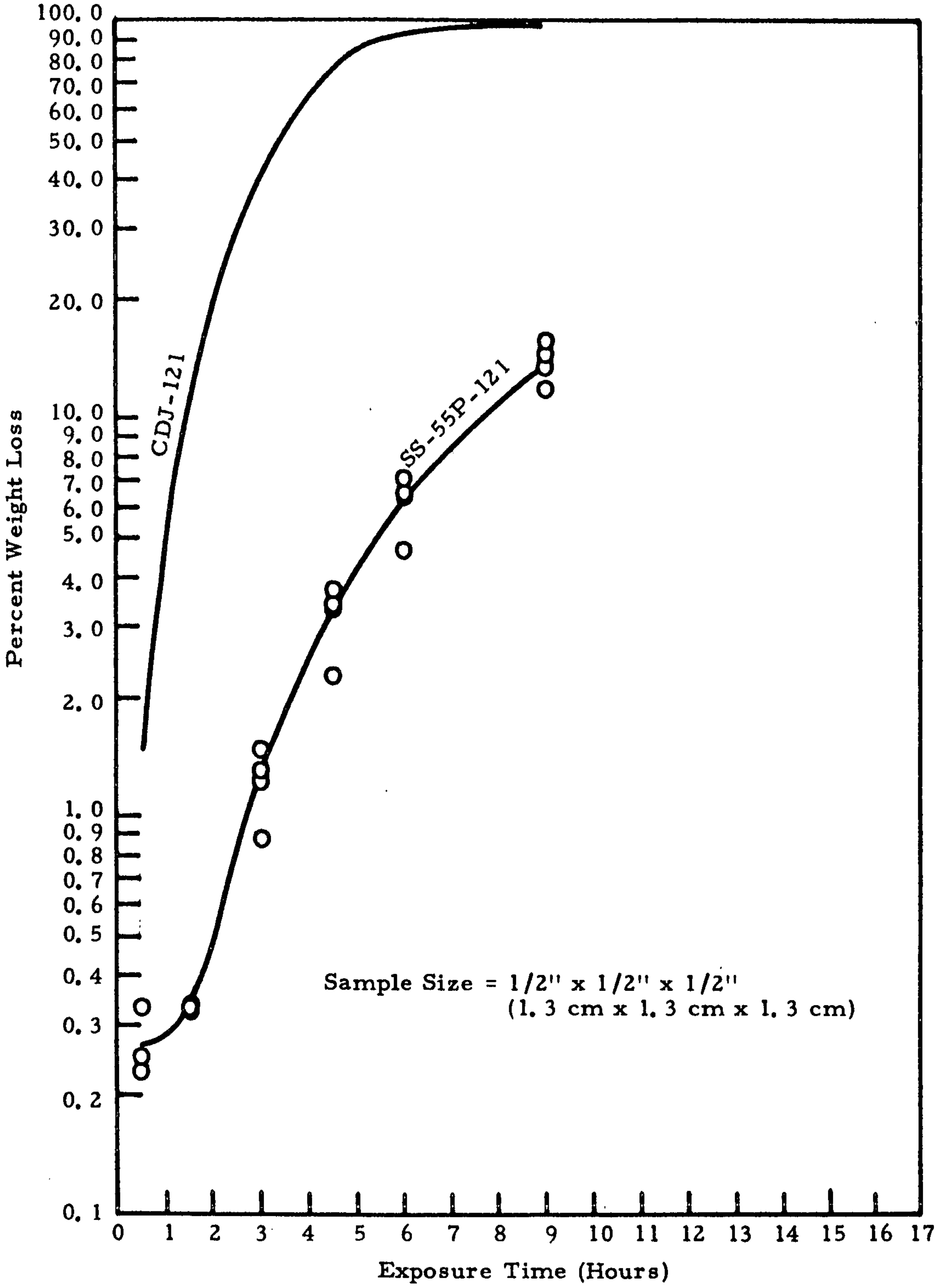
Five oxidation tests were conducted during Task IX by using the No. 121 treated samples. The oxidation study included the testing of two samples of the SS-53A-121 material, three samples of Grade CDJ-121, and four samples of each of the SS-55P-121, SS-56P-121, SS-66P-121, and SS-67P-121 materials. The relative positions of these samples in the furnace were varied during the different tests to avoid any possible position-to-position variation in the oxidizing conditions. All five of the oxidation tests were run for a minimum of nine hours exposure to the oxidizing conditions, with two of the tests being extended to a maximum exposure time of 17 hours. Figures 7 through 11 are semi-logarithmic plots of the average percent weight loss versus exposure time at 1300° F (704° C) for the samples of subsystems SS-53A-121, SS-55P-121, SS-56P-121, SS-66P-121, and SS-67P-121. Each figure includes the control Grade CDJ-121 oxidation curve. The weight losses for all five of the No. 121 treated materials manufactured during Task VIII were significantly lower than that of Grade CDJ-121.

The agreement between the weight losses of the Grade CDJ-121 standards during the oxidation studies of Tasks IV,(11) VII(12) and IX indicate that the results from the three series of tests can be compared directly. Due to the rebuilding of the furnace following the Task I oxidation study,(13) it would be misleading to compare the Task I(10) oxidation test results with those of Tasks IV,(11) VII,(12) and IX.



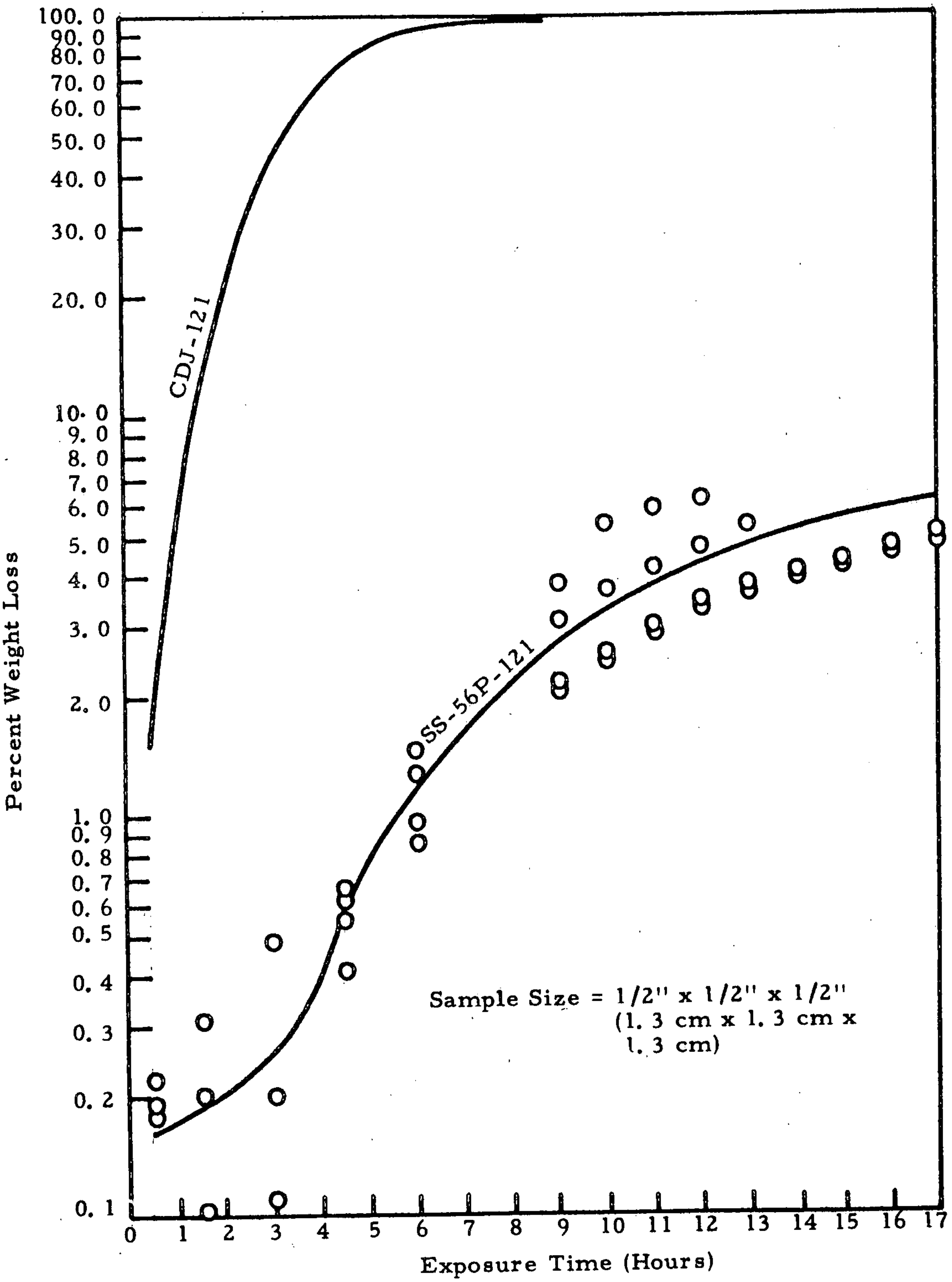
G730006

Figure 7. Percent Weight Loss Versus Exposure Time at 1300° F (704° C)-Subsystem SS-53A-121 Material.



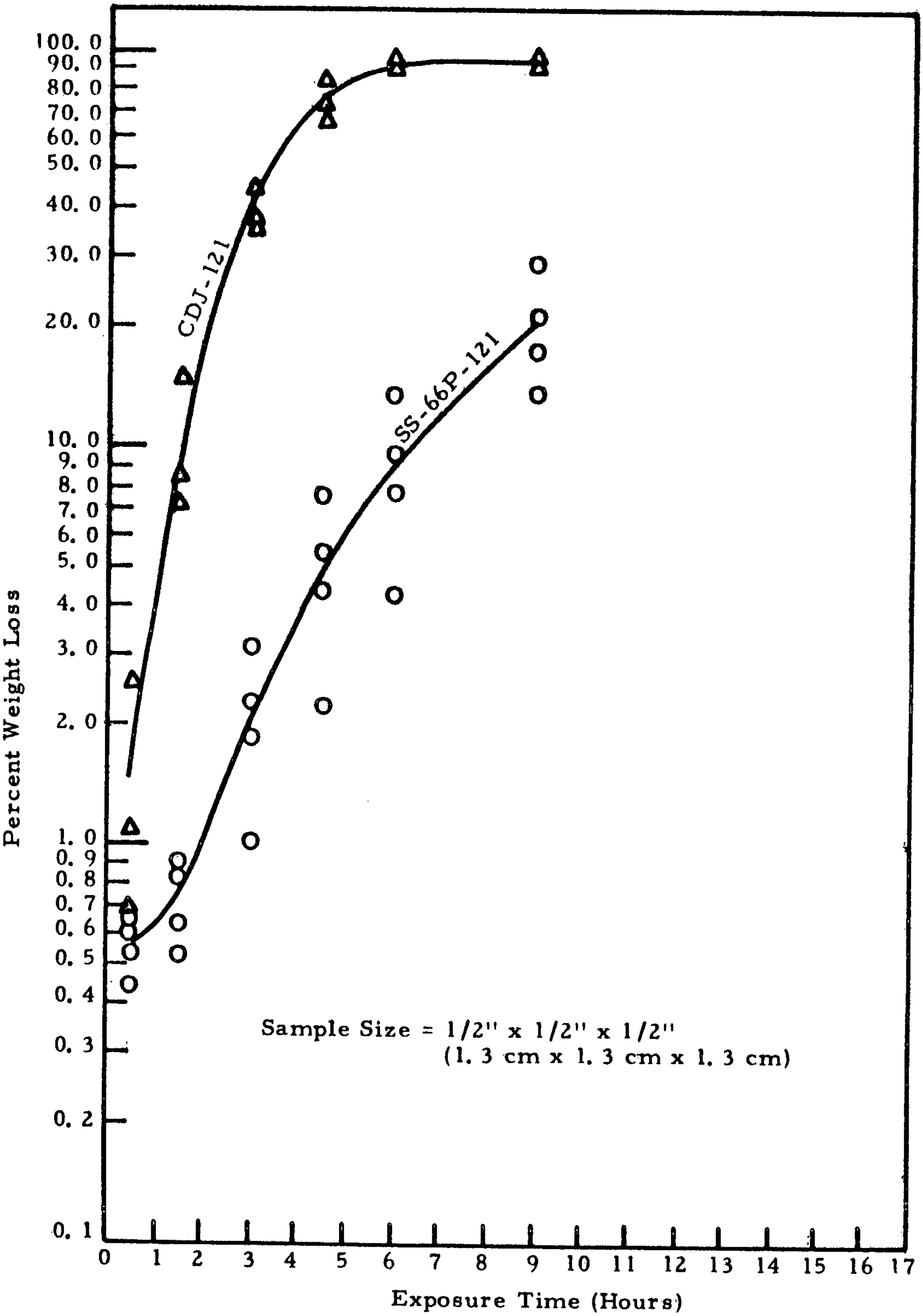
G730007

Figure 8. Percent Weight Loss Versus Exposure Time at 1300°F (704°C)-Subsystem SS-55P-121 Material.



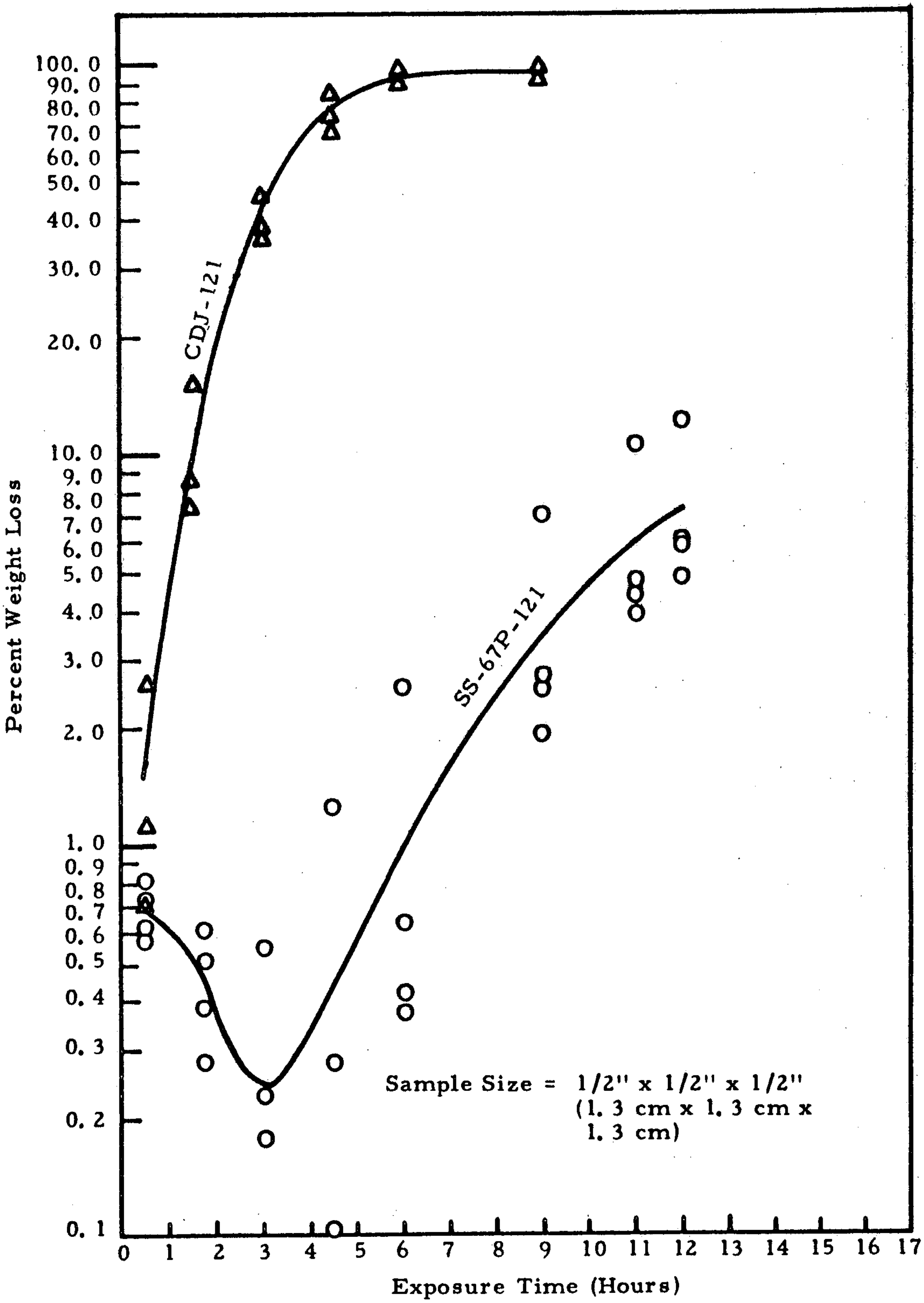
G730005

Figure 9. Percent Weight Loss Versus Exposure Time at 1300° F (704° C)-Subsystem SS-56P-121 Material.



G730004

Figure 10. Percent Weight Loss Versus Exposure Time at 1300° F (704° C)-Subsystem SS-66P-121 Material.



G730003

Figure 11. Percent Weight Loss Versus Exposure Time at 1300° F (704° C)-Subsystem SS-67P-121 Material.

A common method of characterizing the oxidation resistance of a carbon-graphite material is to specify the exposure time at temperature required to produce a five percent weight loss. This technique was used as the basis for comparing the oxidation resistances of the materials characterized during Tasks IV, (11) VII, (12) and IX. The comparison of the oxidation resistances, which is presented in Figure 12, shows that the weight losses of the boronated materials of subsystems SS-55P-121 and SS-66P-121 were similar to those of the more oxidation resistant materials characterized during Tasks IV and VII, (11, 12) whereas the SS-53A-121 material oxidized at a considerably faster rate. Subsystems SS-56P-121 and SS-67P-121 yielded two boronated materials which were considerably more oxidation-resistant than any of the other materials characterized.

The difference between the oxidation resistances of the similar formulation No. IX-121 and subsystem SS-53A-121 materials probably resulted from a difference in the pore size distributions of the two materials. However, mercury intrusion and nitrogen desorption were not employed during this phase of the Contract so the pore structure of the SS-53A material was not examined.

Figure 12 shows that rather large differences existed among the oxidation rates of the materials manufactured from subsystems SS-53A-121, SS-55P-121, SS-56P-121, SS-66P-121, and SS-67-121. A statistical analysis of the oxidation data was conducted to determine if the observed differences were statistically significant. Table XIII lists the differences in percent weight loss measured after 1/2 hour and nine hours exposure to the oxidizing conditions. These differences in weight loss (△ Percent Weight Loss 1/2-9 hours) were used as the basis for the statistical analysis. The exposure time interval used as the basis for the Task IX statistical analysis was approximately three times that (△ Percent Weight Loss 1/2-3 hours) used for the statistical analyses conducted during Tasks IV and VII. (11, 12) The longer exposure time interval was believed to give a more valid comparison of the Task IX oxidation results, but it prevented the inclusion of the materials characterized during the shorter (7 hours maximum) oxidation tests of Tasks IV and VII. (11, 12)

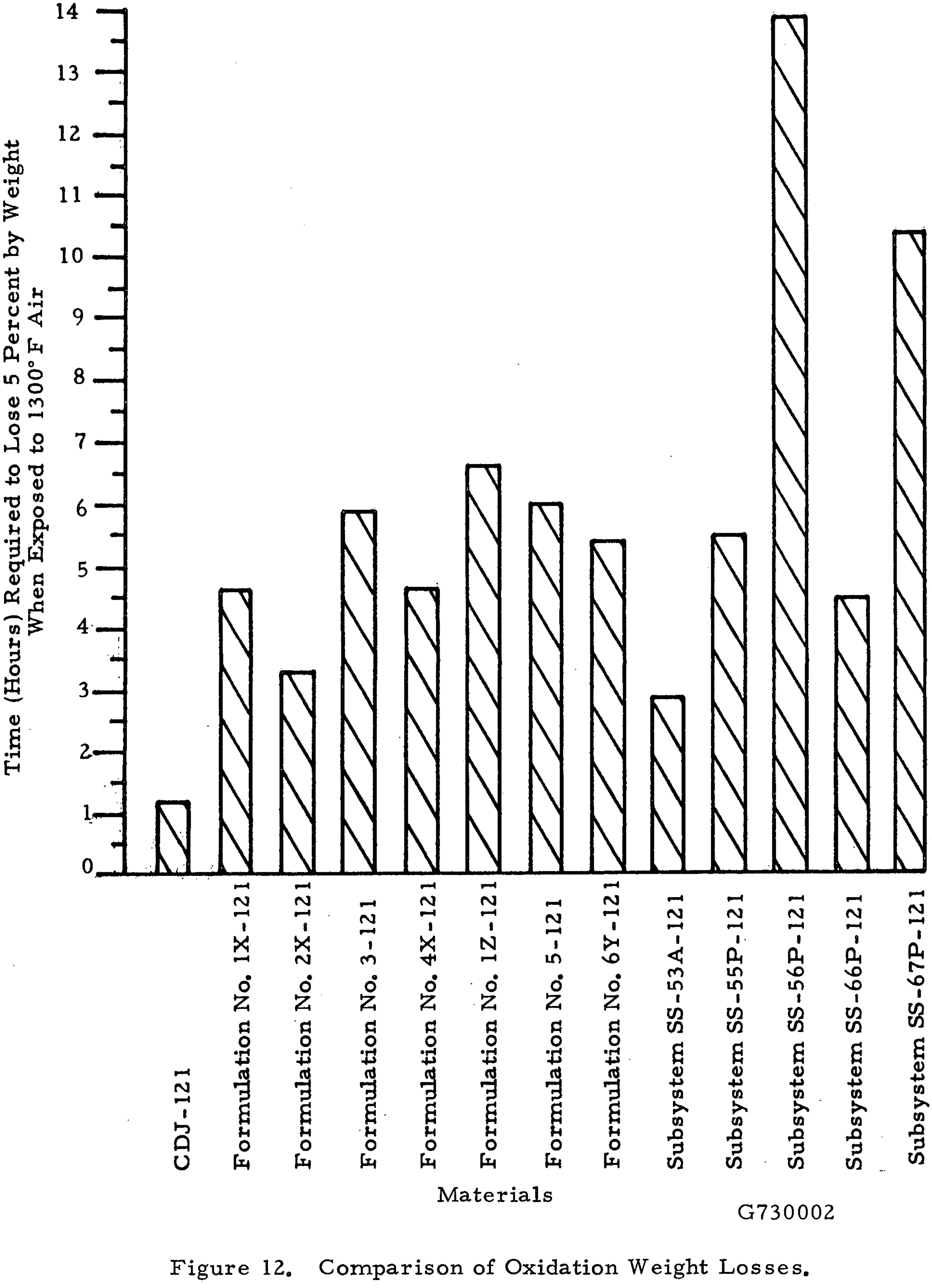


Figure 12. Comparison of Oxidation Weight Losses.

TABLE XIII

Oxidation Test Data for Materials Impregnated with No. 121 Oxidation-Inhibiting Treatment

Δ Percent Weight Loss 1/2-9 hours

	Subsystem SS-53A-121	Subsystem SS-55P-121	Subsystem SS-56P-121	Subsystem SS-66P-121	Subsystem SS-67P-121
Maximum	50.98	15.22	3.62	29.08	6.36
Minimum	49.01	11.69	1.98	13.27	1.38
Average	50.00	13.62	2.61	20.18	2.89
Standard Deviation	1.39	1.50	0.78	6.68	2.33
n	2	4	4	4	4

Statistical Analysis of Oxidation Test Data

	F Distribution			Student's t Distribution				
Materials	F Calculated	F* From Tables	Difference In Variances	t Calculated	Probability	Degrees of Freedom	t** From Tables	Difference Between Oxidation Results
SS-53A-121 vs. SS-55P-121	1.2	4033.0	Not significant	32.27	0.05	4	2.78	Significant
SS-53A-121 vs. SS-56P-121	3.2	25.1	Not significant	80.49	0.05	4	2.78	Significant
SS-53A-121 vs. SS-66P-121	23.6	4033.0	Not significant	5.88	0.05	4	2.78	Significant
SS-53A-121 vs. SS-67P-121	2.8	4033.0	Not significant	26.94	0.05	4	2.78	Significant
SS-55P-121 vs. SS-56P-121	3.7	21.9	Not significant	12.97	0.05	6	2.45	Significant
SS-55P-121 vs. SS-66P-121	20.3	21.9	Not significant	1.89	0.05	6	2.45	Not significant
SS-55P-121 vs. SS-67P-121	2.4	21.9	Not significant	7.74	0.05	6	2.45	Significant
SS-56P-121 vs. SS-66P-121	75.1	21.9	Significant	6.15***	0.05	3***	3.18	Significant
SS-56P-121 vs. SS-67P-121	8.9	21.9	Not significant	0.23	0.05	6	2.45	Not significant
SS-66P-121 vs. SS-67P-121	8.4	21.9	Not significant	4.89	0.05	6	2.45	Significant

---

* Hoel, Paul G., Introduction to Mathematical Statistics, John Wiley & Sons, Inc., New York-London, pages 404 to 407, C1962.

** Brownlee, K. A., Industrial Experimentation, Chemical Publishing Co., Inc., New York, page 144, C1947.

*** Calculated using Behrens-Fisher method.

Note: See Appendix III for explanation of statistical terms.

The procedure of neglecting the results for the first 1/2-hour exposure period was adopted during Task I(10) when the evaporation of absorbed moisture was found to distort the incremental weight losses measured after the first 1/2-hour of exposure. Table XIII also displays the results of the Student's t analyses (14, 15) used to compare the weight losses (△ Percent Weight Loss 1/2-9) determined for the five materials.

The following conclusions were drawn based on the data plotted in Figure 12 and the statistical analysis presented in Table XIII:

1. The addition of boron carbide to the SA-53A base material yielded statistically significant improvements in oxidation resistance.

2. Increasing the boron carbide (B_4C) addition from 5 pbw to 7.5 pbw yielded statistically significant improvements in oxidation resistance.

3. Increasing the final baking temperature of the boronated materials produced decreases in oxidation resistance which were not statistically significant. Although increasing the final baking temperature of the boronated materials increased their degrees of crystallinity as noted in the photomicrographs (Section V-C), it also produced increases in their total porosities as noted in Section V-B. The increase in their total open porosities probably was responsible for the apparent decreased oxidation resistance of the 2800° C baked boronated materials.

The oxidation rates of the samples of subsystems SS-55P-121, SS-56P-121, SS-66P-121, and SS-67P-121 indicate that the four boronated materials are potentially good carbon-graphite seal ring materials. The SS-56P-121 and SS-67P-121 materials are significantly more oxidation-resistant than those previously developed for this Contract.

SECTION VI

SEAL RING CARBON-GRAPHITE MATERIAL FORMULATION

(TASK X)

A. Selection of Four Material Formulations

At the conclusion of Task IX, the Contract Work Plan called for the selection of four approaches to the processing and manufacture of seal ring carbon-graphite bodies. The selection of the four material formulations, which include the required processing techniques, was based on a review of the previous work done under Tasks I through VII(5, 6, 7) and the results of the latest screening study conducted during Tasks VIII and IX. The four selected formulations should yield carbon-graphite seal ring materials which have superior oxidation resistance with strengths and hardness comparable with those of a typical commercial grade.

The screening study conducted during Tasks VIII and IX established the value of using pitch impregnation and the addition of boron carbide to improve the mechanical properties and oxidation resistance of a carbon-graphite material. Subsystem SS-56P-121 yielded a boronated material that was considerably stronger and harder than any of the materials previously developed under Tasks I through VII(5, 6, 7) while being significantly more oxidation resistant. Hence, the SS-56P-121 material was selected as one of the four formulations under Task X. Since increasing the boron carbide content from 5 pbw to 7. 5 pbw produced a significant improvement in oxidation resistance, increasing it again from 7. 5 pbw to 10 pbw might yield another significant improvement. The second formulation selected was, the same as the first except that the boron carbide addition was increased from 7. 5 pbw to 10 pbw. The use of the pitch impregnation and the inclusion of boron carbide (10 percent) in the packing medium during induction baking should prevent the degradation of the mechanical properties encountered during the first attempt at producing a material (SS-57) containing a 10 pbw addition of boron carbide. Section IV-B-2 covered the manufacture and characterization of the SS-57 material.

The third and fourth material formulations selected during Task X were modifications of the resin-bonded formulation No. 6 (composition listed in Table II) from which material was produced during Task VI. (6) The modifications consisted of specifying fine-milled CHP artificial graphite as the major filler component, including boron carbide as an oxidation-inhibiting additive, and incorporating pitch impregnation as a part of the processing. A "fresh" batch of the Bakelite BRP-5095 phenolic resin should be used as the binder for the two new formulations to avoid the processing problems encountered during Task VI. (6)

Table XIV displays the compositions of the four material formulations selected during Task X. A complete description of their processing is presented in the next portion of this section of the report.

B. Processing of the Material Formulations

The following processing steps would be used to produce carbon-graphite seal ring bodies from formulations Nos. 7P, 8P, 9P, and 10P. The finished machined seal rings prepared from these four materials would subsequently be impregnated with the No. 121 oxidation-inhibiting treatment.

1. Formulation No. 7P

a) Blend filler raw materials for one hour.

b) Preheat filler and mixer to 150° C, add pitch, and mix filler and binder in a sigma blade mixer for one hour.

c) Remove hot mix from sigma blade mixer and immediately pass it three times through a pellet mill. This procedure results in thousands of small rods measuring 1/8-inch (0.32 cm) in diameter by 1/8 to 1/2-inch (0.32 to 1.27 cm) in length.

d) Cool pelletized mix to room temperature and micromill.

e) Blend milled material for one hour.

f) Preblend equal amounts (by weight) of the fine-milled boron carbide and the base mix for 1/2 hour by using a twin-shell blender equipped with an intensifier bar.

g) Add remaining requirement of the base mix and blend an additional hour.

TABLE XIV

Identification of the Selected Four Material Formulations

Formulation No.	Base Material Particulate Solid Raw Material	Base Material Binder Raw Material	Additive per 100 pbw Base Material	Impregnants Prior to Final Baking*	Impregnants After Final Baking**
No. 7P-121	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Medium Pitch (70 pph)	Boron Carbide (7. 5 pbw)	Pitch	No. 121 Oxidation-Inhibiting Treatment
No. 8P-121	Fine Milled CHP Artificial Graphite (80 pbw) & Thermax (20 pbw)	No. 30 Medium Pitch (70 pph)	Boron Carbide (10 pbw)	Pitch	No. 121 Oxidation-Inhibiting Treatment
No. 9P-121	Fine Milled CHP Artificial Graphite (80 pbw) & WFA Graphite Fibers (20 pbw)	Bakelite BRP-5095 Resin (70 pph)	Boron Carbide (7. 5 pbw)	Pitch	No. 121 Oxidation-Inhibiting Treatment
No. 10P-121	Fine Milled CHP Artificial Graphite (80 pbw) & WFA Graphite Fibers (20 pbw)	Bakelite BRP-5095 Resin (70 pph)	Boron Carbide (10 pbw)	Pitch	No. 121 Oxidation-Inhibiting Treatment

Note: Final baking temperature = 2200° C.

Proportions are parts by weight (pbw).

Binder proportions are parts (by weight) per 100 parts (by weight) particulate solid raw materials (pph).

Boron carbide additions blended with mixes of base materials just prior to molding "green" compacts.

* Impregnate 1000° C baked compacts with pitch, rebake to 1000° C, and final bake to 2200° C.

** Impregnate with oxidation-inhibiting treatment after desired configuration has been finished machined from 2200° C baked stock.

h) Remove material from blender, pass through a fine mesh screen to break up any remaining lumps of boron carbide, and reblend for 1/2 hour.

i) Warm mold blended material by using a hydraulic press.

j) Pack green compacts with coke in a sagger, place a layer of charcoal on top of the pack, and bake green compacts to 1000° C by using following schedule: rush to 50° C, 50° C to 500° C at 2.5° C per hours, 500° C to 1000° C at 5.0° C per hour, and hold four hours at 1000° C.

k) Impregnate 1000° C baked compacts with pitch and rebake to 1000° C.

l) Pack 1000° C baked compacts in a sealed graphite capsule by using a mixture of 10 percent boron carbide and 90 percent fine coke as the packing medium. Fire the compacts to 2200° C in an induction furnace by using the following schedule: room temperature to 900° C at 400° C per hour, 900° C to 1600° C at 200° C per hour, 1600° C to 2200° C at 300° C per hour, and hold one hour at 2200° C.

2. Formulation No. 8P

The processing of formulation No. 8P is the same as that listed for formulation No. 7P.

3. Formulation No. 9P

a) Blend filler raw materials for one hour. The WFA graphite fibers should be micromilled prior to blending with the fine milled CHP artificial graphite.

b) Dissolve Bakelite BRP-5095 resin binder in equal volume of acetone and mix with filler in a sigma blade mixer for one hour at room temperature.

c) Dry mixed material at 75° C for 16 hours.

d) Crush material by using a hammer pulverizer. The material may still be rather soft and pliable after Step c, due to entrapped acetone, in which case the mix must be chilled at -20° C to harden it before crushing.

e) Place crushed mix in an autoclave and vacuum-evacuate for 16 hours while maintaining the temperature at 50° C. This step will remove the residual acetone.

f) Crush material again by using a hammer pulverizer. This step can be omitted if the mix does not agglomerate during Step e.

g) Micromill crushed material.

h) Blend milled material for one hour.

i) Add boron carbide by using the intensive blending process discussed for formulation No. 7P (Steps f through h).

j) Mold the milled material at room temperature by using a hydraulic press.

k) Pressure cure green compacts at 150° C by using the following procedure: place compacts in autoclave, apply 100 psig (69 N/cm^2) air pressure, rush temperature to 125° C, hold for 1 hour, rush temperature to 150° C, and hold 3 hours. The cure is completed by heating the pressure cured compacts in a circulating-air oven for 1 hour at 100° C, 1 hour at 125° C, and 3 hours at 150° C.

l) Pressure bake cured compacts according to following schedule: rush to 150° C and hold 1/2 hour, raise at 5° C per hour between 150° C and 550° C, and hold at 550° C for 4 hours. During pressure baking, an inert gas should be used to apply 50 to 100 atmospheres pressure.

m) Pack pressure baked compacts with coke in a sagger, place a layer of charcoal on the top of the pack, and bake to 1000° C according to the following schedule: rush to 150° C, raise at 10° C per hour between 150° C and 500° C, hold 2 hours at 500° C, raise at 5° C per hour between 500° C and 1000° C, and hold 4 hours at 1000° C.

n) The remaining processing is the same as that listed for formulation No. 7P, starting at pitch impregnation (Step k).

4. Formulation No. 10P

The processing for formulation No. 10P is the same as that listed for formulation No. 9P.

SECTION VII

DISCUSSION OF THE RESULTS

An overall comparison of the properties of the four boronated materials produced during Task VIII is needed to determine which material is best suited for use as self-acting seals which will be exposed to ambient air temperatures up to 1300° F (704° C). Results from Task IX have shown that all four materials with the No. 121 oxidation inhibiting treatment are significantly more oxidation resistant than commercial Grade CDJ-121. Seal life of all four materials should surpass that of CDJ-121 under high ambient air temperature conditions, where oxidation is the limiting performance factor. Since self-acting seals do experience sliding contact during limited periods of operation, they also require a wear resistant material. High strength, hardness, and modulus are needed to insure good wear resistance. High hardness is also needed to provide erosion resistance which is necessary for self-acting seal materials, since debris passing through the gas film formed between the self-acting seal and seal seat during engine operation tends to score and erode the primary ring. The boronated SS-56P-121 material possesses the best combination of properties for fulfilling the requirements of a self-acting seal material.

The 2200° C baked SS-56P-121 material contains a filler system of fine milled CHP artificial graphite (80 pbw) and Thermax (20 pbw). The material is bonded with No. 30 medium pitch (70 pph) and contains a 7.5 pbw addition of boron carbide for inhibiting oxidation. Intensive mixing and pitch impregnation are included in the processing of the SS-56P-121 material. As the final step in their preparation, the finished machined articles of the SS-56P-121 material are impregnated with the No. 121 oxidation-inhibiting treatment.

The oxidation resistance of the SS-56P-121 material is significantly superior to that of all but one (SS-67P-121) of the other materials. The exposure time needed to produce a five percent weight loss for the SS-56P-121 material when exposed to 1300° F air is approximately 10 times that required for Grade CDJ-121. The superior oxidation resistance of the SS-56P-121 and SS-67P-121 materials results primarily from the 7.5 pbw addition of boron carbide to each material. Subsystem SS-67P-121 is the same as subsystem SS-56P-121 except that the former specifies a final baking temperature of

2800° C rather than 2200° C. A statistical analysis of the oxidation data generated during Task IX has shown that the SS-56P-121 and SS-67P-121 materials are significantly more oxidation-resistant than the similar SS-55P-121 (2200° C baked) and SS-66P-121 (2800° C baked) materials which contain 5 pbw additions of boron carbide. The SS-55P-121 and SS-66P-121 materials have oxidation resistances comparable with those of the more oxidation-resistant materials manufactured during Tasks III and VI.(6, 7) Although the oxidation resistance of the SS-67P-121 material is comparable with that of the SS-56P-121 material, the mechanical properties of the former material are rather poor. The SS-67P-121 material thus would not be a good self-acting seal material, since it would probably possess inadequate wear-and erosion-resistance properties.

The use of a fine milled particulate graphite, intensive mixing, pitch impregnation, and a boron diffusion preventative pack during final baking all helped to produce the superior mechanical properties of the SS-55P, SS-56P, and SS-66P materials. The 6000 psi (4130 N/cm^2) average flexural strengths and 2.5×10^6 psi ($1.7 \times 10^6 N/cm^2$) average elastic moduli of the three boronated materials approached the corresponding 8800 psi (6100 N/cm^2) and 3.2×10^6 psi ($2.2 \times 10^6 N/cm^2$) values for commercial seal ring Grade CDJ. Although the three boronated materials are not so hard as Grade CDJ (105 Rockwell "E"), they are considerably harder than any of the other materials developed for this Contract. Subsystems SS-55P and SS-56P yield materials having Rockwell "S" hardnesses of 110, whereas the SS-66P material is slightly softer (96 Rockwell "S"). The highest average flexural strength and hardness recorded for any of the other materials developed for this Contract are 4750 psi (3270 N/cm^2) and 88 Rockwell "S". The subsystems SS-55P, SS-56P, and SS-66P materials should be the most wear and erosion resistant due to their improved mechanical properties.

The properties of the subsystems SS-55P-121, SS-56P-121, and SS-66P-121 materials have been examined and the materials ranked as to their suitability for fulfilling the goal of this Contract. These three boronated materials rank ahead of all the other materials produced during Tasks III and VI,(6, 7) since the three materials possess significantly improved mechanical properties with oxidation resistances similar to those of the previous materials. Due to its poor mechanical properties, the oxidation-resistant SS-67P-121 material is not included in the ranking. The three boronated materials were ranked in the following order of decreasing suitability:

1. Subsystem SS-56P-121,
2. Subsystem SS-55P-121, and
3. Subsystem SS-66P-121.

Subsystem SS-56P-121 is listed first, since it yields a material that is significantly more oxidation-resistant than the other two materials while possessing similar mechanical properties. The subsystem SS-55P-121 material is listed second, since it is slightly harder than the SS-66P-121 material and thus may possess a slight advantage in wear and erosion resistance. No significant difference exists between the oxidation resistances of the SS-55P-121 and SS-66P-121 materials.

APPENDIX I

PROCEDURES USED TO CHARACTERIZE RAW MATERIALS

Helium Density - Measured with Beckman pycnometer

Surface Area - B. E. T. method

Screen Analysis - Tyler standard screen sieve analysis

Chemical Analysis - Ash measured per ASTM C561 except 680° C overnight

Moisture measured by drying at 105° C overnight (Modification of ASTM C562)

Emission Spectrographic Analysis - Conducted using Jerrell Ash emission spectrograph

Coking Value - Modified Conradson technique (ASTM D-189-52). Modification is furnace instead of gas burner for heat

Benzene Insoluble - Method based on ASTM D2317

Quinoline Insoluble - Method based on ASTM D2318

Softening Point - Method based on ASTM D2319

Elemental Chemical Analysis - (C) Combustion techniques using gravimetric analysis

(H) Combustion techniques using gravimetric analysis

(O) LECO oxygen analyzer

(N) Kjeldahl method

(S) X-ray fluorescence

Differential Thermal Analysis - Mettler thermal analyzer

Thermal Gravimetric Analysis - Mettler thermal analyzer

APPENDIX II

PROCEDURES USED TO MEASURE MATERIAL PROPERTIES

Bulk Density -	Determined by direct physical measurement of mass and volume.
Helium Density -	Measured with Beckman pycnometer.
Flexural Strength -	ASTM C651-70 through use of a 4.5-inch x 1.0-inch x 0.5-inch (11.4 cm x 2.5 cm x 1.3 cm) ground sample.
Elastic Modulus -	Determined by a sonic resonance method by utilizing a variable frequency oscillator, amplifier, frequency counter, oscilloscope, filter, and transmitting and receiving transducers. Measured at room temperature by using a 4.5-inch x 1.0-inch x 0.5-inch (11.4 cm x 2.5 cm x 1.3 cm) ground sample.
Hardness -	Measured with a Rockwell Hardness Tester by using a 0.5-inch (1.3 cm) diameter ball, a 100 Kg major load, and the R_s scale.
Thermal Conductivity -	Calculated from a measured thermal diffusivity by using a sample of known density and specific heat. Thermal diffusivity is measured by a laser flash method by using a pulsed ruby laser with associated mirrors, filters, thermocouples, oscilloscopes, and camera. Measured at room temperature by using a 0.5-inch (1.3 cm) diameter x 0.080-inch (.20 cm) thick sample.
Coefficient of Thermal Expansion -	Measured by an elongation method by using a tube furnace, twin telescopes, thermocouples and optical pyrometers. This measurement was carried out from room temperature to 1000° C in an argon atmosphere by using a 0.5-inch x 0.5-inch x 2.5-inch (1.3 cm x 1.3 cm x 6.4 cm) ground sample

APPENDIX II (Cont'd)

Pore Volume and Distribution by Mercury Intrusion -	The sample is placed in a chamber and evacuated. Mercury from an external reservoir is induced into the sealed chamber as the system is allowed to return to atmospheric pressure. When equilibrium is reached, increasing amounts of pressure are applied to the mercury in the reservoir and the corresponding changes in the volume of the mercury in the reservoir are recorded as the mercury is intruded into the sample. Knowing the corresponding reservoir volume and pressure changes allows one to calculate the pore volume and distribution of the sample, since the size of the pores filled by mercury is inversely proportional to the applied pressure. Mercury does not wet carbon-graphite material.
Pore Volume of Nitrogen Desorption -	The volume of pores smaller than 600Å in diameter was determined from the nitrogen desorption isotherm by using the exact form of the equation attributed to Barrett, Joyner, and Halenda(16, 17) with no simplifying assumptions.

APPENDIX III

DEFINITION OF STATISTICAL TERMS

F Distribution (15)

$$F_{\text{calculated}} = \frac{\hat{\sigma}_x^2}{\hat{\sigma}_y^2}$$

Where, $\hat{\sigma}_x^2$ and $\hat{\sigma}_y^2$ are unbiased estimates of the two sample variances. The expression $\hat{\sigma}_x^2$ will always denote the larger of the two estimates.

$$\hat{\sigma}_x^2 = \frac{\sum_{i=1}^{n_x} (x_i - \bar{x})^2}{n_x - 1}$$

Where $\bar{x} = \dfrac{\sum_{i=1}^{n_x} x_i}{n_x}$; n_x is the size of the random samples.

Similarly:

$$\hat{\sigma}_y^2 = \frac{\sum_{i=1}^{n_y} (y_i - \bar{y})^2}{n_y - 1} .$$

After the value of F is calculated, it is compared with the 2.5% critical value of F obtained from a statistical F distribution table. To determine the 2.5% critical value of F from the table, one must know the two degrees of freedom. The two degrees of freedom are calculated as follows:

$$v_1 = n_x - 1 \text{ and}$$

$$v_2 = n_y - 1.$$

The 2.5% critical value of F is for a double tail analysis at a 95% confidence level. If the calculated value of F is less than the 2.5% critical value of F obtained from the statistical table, the Student's t distribution can be used to compare the means of the two samples as follows.

Student's t Distribution (14, 15)

The Student's t distribution is used to determine whether the mean of one sample is significantly different from the mean of a second sample, or whether the two sample means can be regarded as drawn from one population.

$$\bar{x} = \frac{\sum_{i=1}^{n_x} x_i}{n_x}, \quad \bar{y} = \frac{\sum_{i=1}^{n_y} y_i}{n_y}$$

Where $\bar{x}$ is the larger of the two sample means.

$$\sigma^2 = \frac{\left[\sum_{i=1}^{n_y} (y_i^2) - \frac{\left(\sum_{i=1}^{n_y} (y_i)\right)^2}{n_y} + \sum_{i=1}^{n_x} (x_i^2) - \frac{\left(\sum_{i=1}^{n_x} (x_i)\right)^2}{n_x}\right.}{(n_x + n_y - 2)}$$

$$t_{\text{calculated}} = \frac{\bar{x} - \bar{y}}{\sigma} \sqrt{\frac{n_x \cdot n_y}{n_x + n_y}}$$

After the value of t is calculated, it is compared to the value of t obtained from a statistical t distribution table. To obtain the value of t from the table, one must calculate the degrees of freedom by using the following equation:

Degrees of freedom $= n_x + n_y - 2$.

After the degrees have been calculated, the corresponding value of t can be found in the table by using a value of P (probability) equal to 0. 05 for a single tail analysis at a 95% confidence level. The difference between the means of the two sample populations is significant only if the calculated value of t is greater than the value of t from the table. That is:

$t_{\text{calculated}} > t_{\text{table}}$ = significant;

$t_{\text{calculated}} < t_{\text{table}}$ = not significant.

Behrens - Fisher Problem(15)

When the calculated value of F is greater than the 2.5% critical value of F obtained from a statistical F distribution table, an approximate value of t is calculated by using the following equation in which μ_x is assumed to equal μ_y:

$$t = \frac{(\bar{x} - \bar{y}) - (\mu_x - \mu_y)}{\sqrt{\frac{\hat{\sigma}_x^2}{n_x} + \frac{\hat{\sigma}_y^2}{n_y}}}$$

Where μ_x and μ_y are the means of the total populations from which the sample populations (x and y) are taken.

After the approximate value of t is calculated, it is compared with the value of t obtained from a statistical t distribution table by using the degrees of freedom (v) calculated from the following equation:

$$v = \frac{\left(\frac{\hat{\sigma}_x^2}{n_x} + \frac{\hat{\sigma}_y^2}{n_y}\right)^2}{\frac{\left(\frac{\hat{\sigma}_x^2}{n_x}\right)^2}{n_x + 1} + \frac{\left(\frac{\hat{\sigma}_y^2}{n_y}\right)^2}{n_y + 1}} - 2$$

The difference between the means of the two sample populations is significant only if the calculated approximate value of t is greater than the value of t from the table.

REFERENCES

1. Parks, A. J., McKibbin, R. H., and Ng, C. C. W., "Development of Main Shaft Seals for Advanced Air Breathing Propulsion Systems," NAS3-7609, Final Report Phase I (August, 1967), NASA CR-72338, page 49.
2. Johnson, Robert L., and Ludwig, Lawrence P., "Shaft Face Seal with Self-Acting Lift Augmentation for Advanced Gas Turbine Engines," NASA-TN-D-5170, NASA Lewis Research Center, Cleveland, Ohio, April, 1969.
3. Strom, Thomas N., Allen, Gordon P., and Johnson, Robert L., "Wear and Friction of Impregnated Mechanical Carbons at Temperatures to 1400° F (760° C) in Air or Nitrogen, "NASA-TN-D-3958, page 2, NASA Lewis Research Center, Cleveland, Ohio May, 1967.
4. Lauzau, W. R., Shelton, B. R., and Waldheger, R. A., "The Use of Carbon-Graphite in Mechanical Seals," Lubrication Engineering, Volume 19, pages 201-209, May, 1963.
5. Fechter, N. J., and Petrunich, P. S., "Development of Seal Ring Carbon-Graphite Materials (Tasks I and II)," Union Carbide Corporation, Topical Report NASA CR-72799 (Contract NAS3-13211), January, 1971.
6. Fechter, N. J., and Petrunich, P. S., "Development of Seal Ring Carbon-Graphite Materials (Tasks III and IV)," Union Carbide Corporation, Topical Report NASA CR-72986 (Contract NAS3-13211), August, 1971
7. Fechter, N. J., and Petrunich, P. S., "Development of Seal Ring Carbon-Graphite Materials (Tasks V, VI, and VII)," Union Carbide Corporation, Topical Report NASA CR-120955 (Contract NAS3-13211), August, 1972.
8. The Industrial Graphite Engineering Handbook, Union Carbide Corporation, pages 5A. 08. 02-5A. 08. 03, C1969.
9. Allardice, D. J. and Walker, P. L. Jr., "The Effect of Substitutional Boron on the Kinetics of the Graphite-Oxygen Reaction, "Defense Ceramic Information Center; Summary of papers for Ninth Biennial Conference on Carbon, Co-sponsored by the American Carbon Committee and Boston College, Chestnut Hill, Massachusetts, page 113, June 16-20, 1969.

10. Loc. cit., Reference 5, pages 84-89.

11. Loc. cit., Reference 6, pages 77-87.

12. Loc. cit., Reference 7, pages 83-91.

13. Loc. cit., Reference 6, page 79.

14. Brownlee, K. A., Industrial Experimentation, Chemical Publishing Co., Inc., New York, pages 28-32, C1947.

15. Hoel, Paul G., Introduction to Mathematical Statistics, John Wiley & Sons, Inc., New York- London, pages 271 to 288, C1962.

16. Barrett, E. P., Joyner, L. G., and Halenda, P. B., The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, Journal of the American Chemical Society, Volume 73, page 373, 1951.

17. Roberts, B. F., A Procedure for Estimating Pore Volume and Area Distributions by Sorption Isotherms, Journal of Colloid and Interface Science, Volume 23, pages 266-273, 1967.

DISTRIBUTION LIST

	Addressee	No. of Copies
1.	NASA Headquarters	
	Washington, D. C. 20546	
	Attn: N. F. Rekos (RL)	1
	A. J. Evans (RH)	1
	J. Maltz (RMW)	1
	J. J. Gangler (RRM)	1
2.	NASA Lewis Research Center	
	21000 Brookpark Road	
	Cleveland, OH 44135	
	Attn. A. Ginsburg, MS 5-3	1
	E. E. Bisson, MS 5-3	1
	C. H. Voit, MS 5-3	1
	B. Lubarsky, MS 3-3	1
	R. J. Paginton, MS 500-206	1
	L. W. Schopen, MS 500-206	1
	R. L. Johnson, MS 23-2	1
	M. A. Swikert, MS 23-2	1
	W. R. Loomis, MS 23-2	1
	L. P. Ludwig, MS 23-2	6
	Report Control Office, MS 5-5	1
	Library, MS 60-3	1
	Technology Utilization Office, MS 3-19	1
3.	NASA Scientific and Technical Information Facility	
	P. O. Box 33	
	College Park, MD 20740	
	Attn: NASA Representative	2
4.	NASA Langley Research Center	
	Langley Station	
	Hampton, VA 23365	
	Attn: Mark R. Nichols	1
5.	Wright-Patterson Air Force Base	
	Dayton, OH 45433	
	Attn; AFAPL (APFL), K. L. Berkey and L. DeBrohum	1
	AFAPL (AFTC), C. Simpson	1
	APTP, I. J. Gershon	1
	SESHS, J. L. Wilkins	1
	SEJDF, S. Prete	1
	MANE, R. Headrick	1
	MANE, P. House	1
	AFML/XR, R. L. Adamczak	1