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THE PRESSURE-CARBONIZATION OF CARBON BONDED SILICON CARBIDE-GRAPHITE FOR USE IN UNCOOLED ROCKET NOZZLES

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FOREWORD

This report was prepared by Alfred University under USAF Contract No. AF33(616)2007. The contract was initiated under Project No. 7350, "Ceramic and Cermet Materials", Task No. 73500, "Ceramic and Cermet Materials Development", formerly RDO No. 619-11, "Substitutes for Critical and Strategic Materials", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with 2/Lt Normand Hyman acting as project engineer.

ABSTRACT

The resistance to flame erosion of Alfred 410, a carbon bonded SiC-Graphite composition, was improved by the substitution of larger grain sized SiC for the "settling tank fines" previously used. A new method of forming and firing carbon bonded SiC-Graphite was developed in which the material was carbonized under pressure in stainless steel dies. The process resulted in a product with 15% higher density and 40% lower porosity than that previously obtained. This improvement in properties also resulted in greater resistance to flame erosion.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
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I INTRODUCTION

Silicon carbide-graphite, bonded by carbon, is exceptionally resistant to failure from thermal shock and high temperature, high velocity gas erosion. In a previous investigation, a composition was developed in which the carbon bond was achieved by the carbonization of tar and pitch and oxidation resistance obtained by the incorporation of silicon in the mix. The silicon oxidized to silica on the surface and melted, forming an extremely viscous coating when subject to the high temperature of the rocket motor combustion products. This material was designated Alfred 410 and its composition is included in Table I.

In previous work, Alfred 410 was fabricated by heating the well mixed powder and tar to a temperature of 300°F and shaped either by tamping or pressing in steel dies. The parts were packed in graphite grain for oxidation protection and carbonized to 1830°F to drive off the volatiles from the tar and pitch, and to set the residual carbon bond. This process resulted in a part having a porosity of approximately 25%.

The purpose of the work reported here was to improve the Alfred 410 type of material by two studies: (1) the carbonization and graphitization of the material under pressure; a low temperature modification of hot pressing; (2) the investigation of the effect of silicon carbide grain and the ratio of graphite to silicon carbide.

If a carbon bonded material could be carbonized under pressure, it was thought that as the volatiles left the part the pressure would close some of the resulting pores and a more dense and uniform part would be produced.

The effect of silicon carbide grain size and the ratio of silicon carbide to graphite had not been determined using a laboratory rocket test for evaluation.

II PROCEDURE AND RESULTS

A. Effect of SiC Grain Size and SiC-Graphite Ratio

In Alfred 410 the silicon carbide used was that generally referred to as "settling tank fines," a very fine grained, impure material. The ratio by weight of silicon carbide to graphite was three to one. The use of settling tank fines and the 3:1 SiC-Graphite ratio was established at a time when a laboratory rocket test stand was not available to evaluate the complex property of resistance to high velocity, high temperature, flame erosion.

In the present experiments a series of five compositions were selected for study, Table I, including Alfred 410. In composition 451, the ratio of settling tank fines silicon carbide to graphite was changed to 1:1 by weight. In composition 556, a larger grained silicon carbide, 50 to 100 mesh was substituted for the greater part of the settling tank fines-silicon carbide in composition 410. In composition 558, the changes from settling tank fines to larger grained silicon carbide and the SiC to graphite ratio from 3:1 to 1:1 were both incorporated into one composition. In composition 558A one further change was made in that a 3:1 pitch-tar ratio was used, rather than the original 1:1 ratio.

Increasing the ratio of pitch to tar in the composition resulted in a more difficult forming procedure but a higher residual carbon bond content.

Testing - These compositions were studied using the laboratory propane-oxygen test motor, hereafter referred to as XMRM-2, as the only physical test.

The XMRM-2 laboratory test motor is shown in Fig. 1. It consists of a system for metering and mixing propane and oxygen, injecting this mixture through twelve 0.030 inch diameter holes in a water cooled injection plate into a miniature rocket chamber and nozzle. The test chamber and nozzle is one inch I.D., two inches O.D. The results of this test have been correlated several times with the results of full scale 1000 lb. thrust testing at WADC.

Each of the nozzles fabricated from the compositions shown in Table I were subjected to repeated firings of two and one-half minute duration. Temperatures of between 4000°F and 4500°F were observed by an optical pyrometer on the nozzle section of the part.

The throat area of each nozzle was measured before and after testing by a method in which a nearly parallel beam of light was directed through the nozzle and then

TABLE I

Composition - Percent by Weight

Comp.	SiC(S.T.F.*)	SiC(50-100m)	Graphite †	FeMo	Pitch	Tar	Silicon
410	52.0	----	17.6	0.4	10.0	10.0	10.0
451	34.8	----	34.8	0.4	10.0	10.0	10.0
556	7.8	44.2	17.6	0.4	10.0	10.0	10.0
558	5.2	29.6	34.8	0.4	10.0	10.0	10.0
558A	5.2	29.6	34.8	0.4	15.0	5.0	10.0

*S.T.F. - Settling Tank Fines, approximately 85% SiC

†Joseph Dixon Crucible Grade 1101

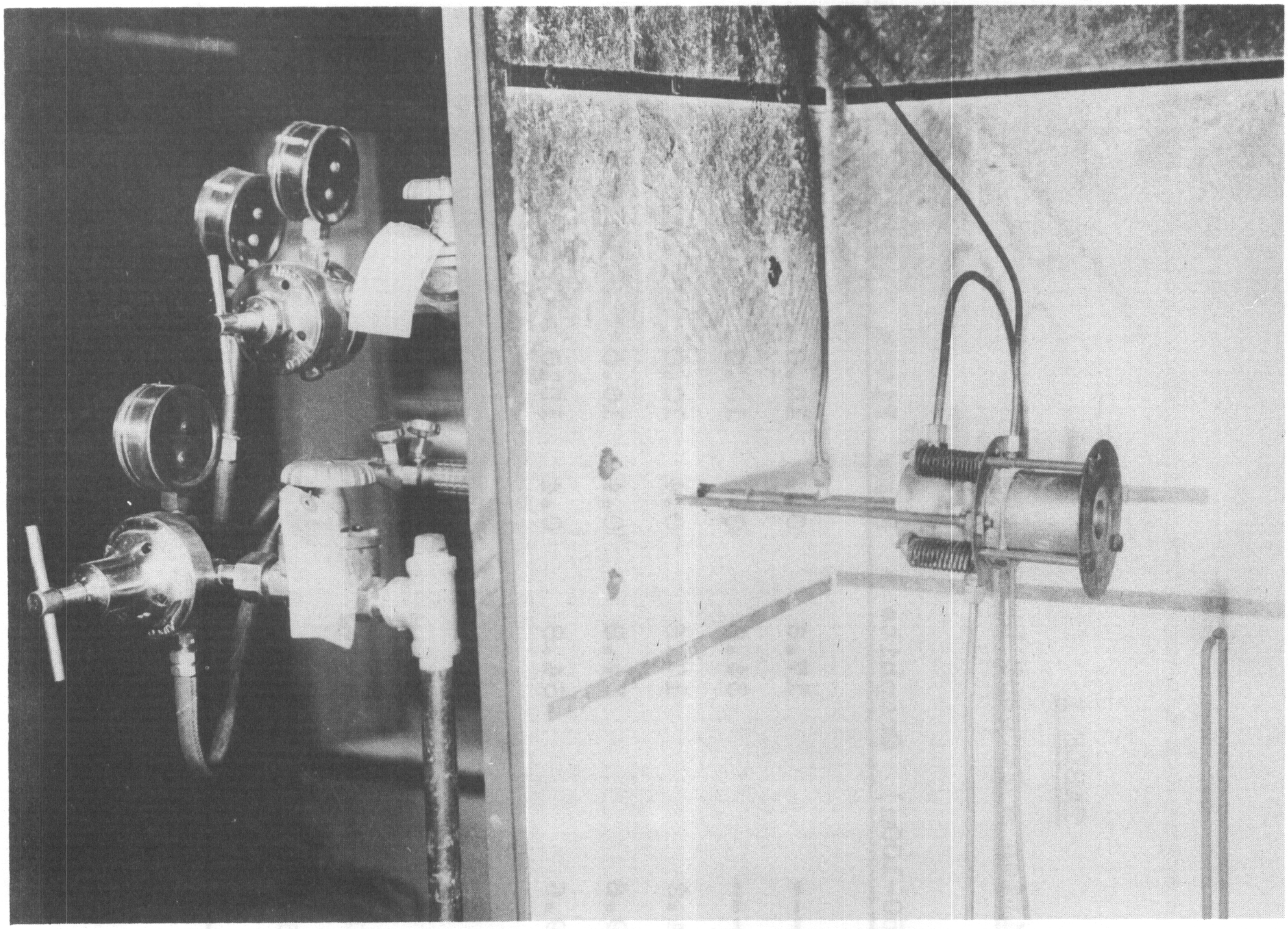

Fig. 1

XMRM-2 TEST MOTOR

projected on a ground glass plate where the area could be measured with a planimeter. Seven nozzles of each composition were tested.

The area enlargement data obtained are given in Table II and will be discussed later in the report.

B. Carbonization and Graphitization of Alfred 410 Under Pressure

The term "carbonization" is used here to designate the process by which the volatiles are driven off the tar and pitch and a residual carbon bond formed. The term "graphitization" refers to the crystallization of carbon into the graphite structure. Carbonization in general, can be said to take place between room temperature and 1830°F, while graphitization takes place between 1830°F and 4700°F or higher. This is obviously an oversimplification.

Alfred 410, carbonized by packing the tamped or pressed parts in graphite and heating to 1832°F, had a density of approximately 1.9 gm/cc and a porosity of 25%.

In all preliminary work of carbonizing under pressure, Body 410, with the substitution of pitch for tar, was used exclusively. Before any attempt was made to produce laboratory test nozzles, considerable work was done to ascertain the characteristics of the material when subjected to pressure during the heating cycle. In carrying out this phase of the investigation, two hot-pressing furnaces were employed: an induction heated furnace, Fig. 2, and a globar heated furnace, Fig. 3. Both furnaces produced approximately the same results, even though the induction furnace had a considerably faster heating rate. This indicated that when heating under pressure, the rate of heating was not an important factor. Early work carried on by this laboratory showed that in the old method of fabrication, a firing rate of 90°F/hr., as compared to 270°F/hr. had a marked effect on the increase in density and strength of the finished product.

Initially graphite dies were used in pressing simple shapes such as discs. Alfred 410 parted easily from the graphite die after firing. However, graphite dies of a more complicated nature, necessary for the pressing of laboratory test nozzles, were not structurally practical and presented problems in parting not easily overcome. Stainless steel dies were obtained and proved to be successful.

TABLE II

PERCENT AREA ENLARGEMENT

	Duration of Burst (minutes)			
Composition	2 1/2	5	7 1/2	10
410	10.04	17.35	21.80	--
541	13.28	28.07	40.80	--
556	5.14	11.43	15.77	23.36
558	3.75	9.14	16.03	22.90
558A	5.32	10.65	13.57	22.20

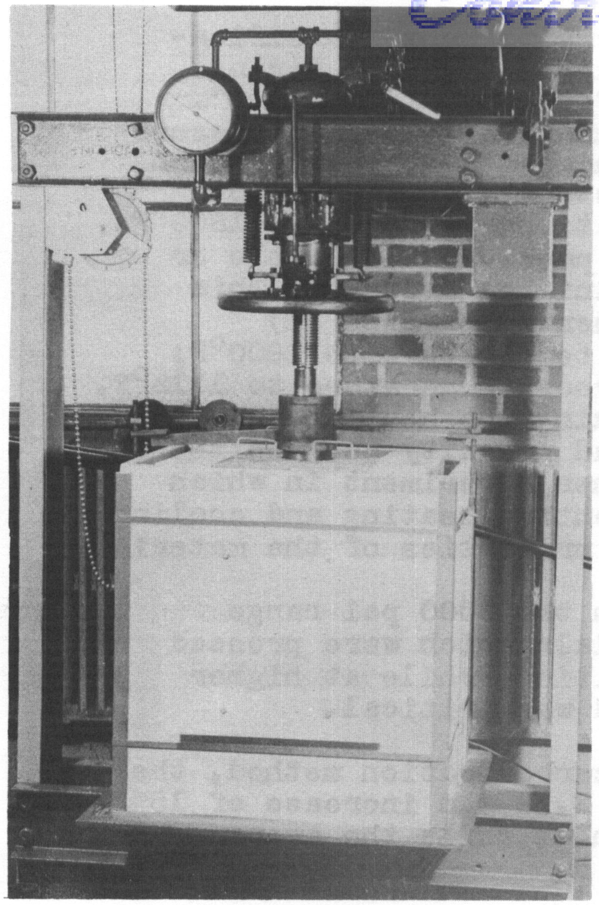

Fig. 2

Induction Heated Press

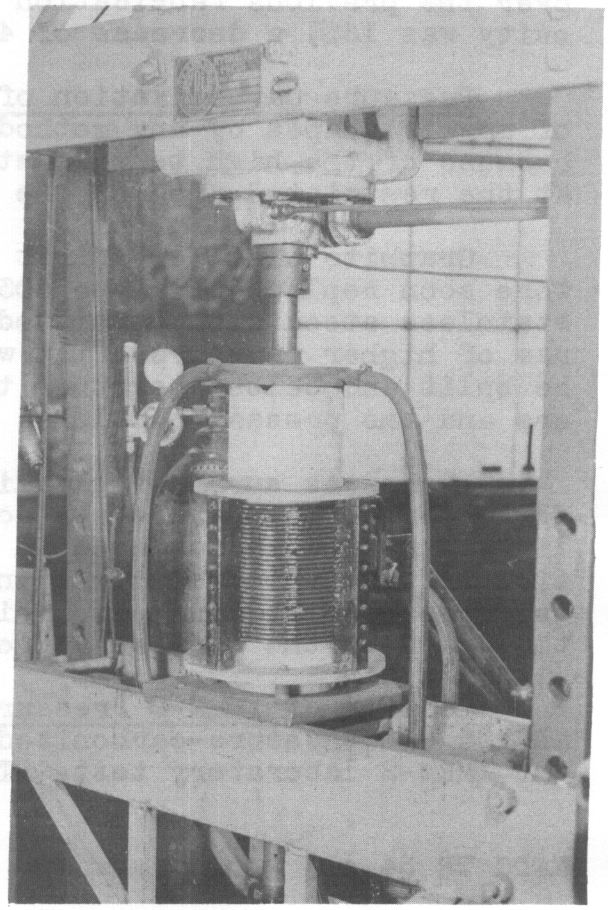

Fig. 3

Globar Heated Press

In establishing the range where the most densification or slump of the material occurred, several firings were made employing an Ames Dial for recording "slump". It was found that densification, under a constant pressure from room temperature to 1832°F increased sharply between 140-200°F, continued to increase steadily between 200-1000°F, and appeared to remain stationary from 1000-1800°F. This indicated that above 1000°F, pressure had little or no effect on the density of the finished product. This was later substantiated by experiments in which (1) pressure was maintained from room temperature to 1800°F; (2) pressure was maintained from room temperature to 1112°F, releasing the pressure and continuing the heating to 1800°F. No noticeable effect of density and porosity between the two methods was observed. A further experiment in which pressure was maintained over the entire heating and cooling cycle did not change the physical properties of the material.

It was found that pressure in the 3000 psi range produced the best results. Materials which were pressed at lower pressures had lower densities, while at higher pressures the strength of the mold was critical.

By the use of this pressure-carbonization method, the average bulk density attained was 2.18, an increase of 15% over the previous fabrication method; while the average porosity was 15%, a decrease of 40%.

Pressure Carbonization of XRM-2 Nozzles - The forming of nozzle shapes by any method of hot pressing is difficult because of the high tensile stresses generated in the mandrel at the restricted area of the nozzle.

Graphite dies were first used for this purpose, but were soon replaced by Type 303 Stainless Steel dies. The stainless steel dies permitted a smaller die O.D. and the use of higher pressures. It was found that the die had to be split and bolted together to permit removal of the plungers and the pressed nozzle.

There was surprisingly little adherence of the Alfred 410 material to the die surfaces during carbonization. One difficulty was encountered in that the differential contraction of the stainless steel and Alfred 410 on cooling caused the nozzle to be crushed. This was overcome by stripping the die from the part at approximately 570-750°F.

Testing of XMRM-2 Pressure-Carbonized Nozzles - Six Alfred 410 pressure-carbonized nozzles were evaluated in the XMRM-2 laboratory test. The resulting area enlargement is shown in Table III. The average area enlargement encountered in multiple bursts of both the pressure-carbonized nozzles and those produced by cold pressing from the various compositions is plotted in Fig. 4.

TABLE III

PERCENT AREA ENLARGEMENT

PRESSURE CARBONIZATION

COMPOSITION 410

Time of Fire (Minutes)	% Area Enlargement
2 1/2	8.13
5	10.10
7 1/2	11.33
10	13.13

Graphitization Under Pressure - Alfred 410 was hot pressed to temperatures of 3100°F, well into the graphite forming range, and even higher densities were obtained. However, the actual values obtained were later found to be in error because of contamination of the SiC used by alumina. The work was not repeated with reliable materials since the process was impractical from a production standpoint and time was limited.

C. Polishing and Etching Technique for Metallographic Determinations

Because of the soft carbon matrix, the polishing of samples of carbon bonded silicon carbide was extremely difficult. A method was developed whereby the "pulling out" of the silicon carbide grains from the soft carbon matrix was successfully eliminated. The procedure was as follows: a mixture of 10% Aroclor 4465 (Monsanto Chemical Co.) and 90% by weight of powdered sulfur flowers was heated in a beaker until completely melted. A suitable sample was cut with a diamond cut-off wheel, placed in the hot mixture, and the beaker placed in a desiccator and evacuated. Just before the melt reached

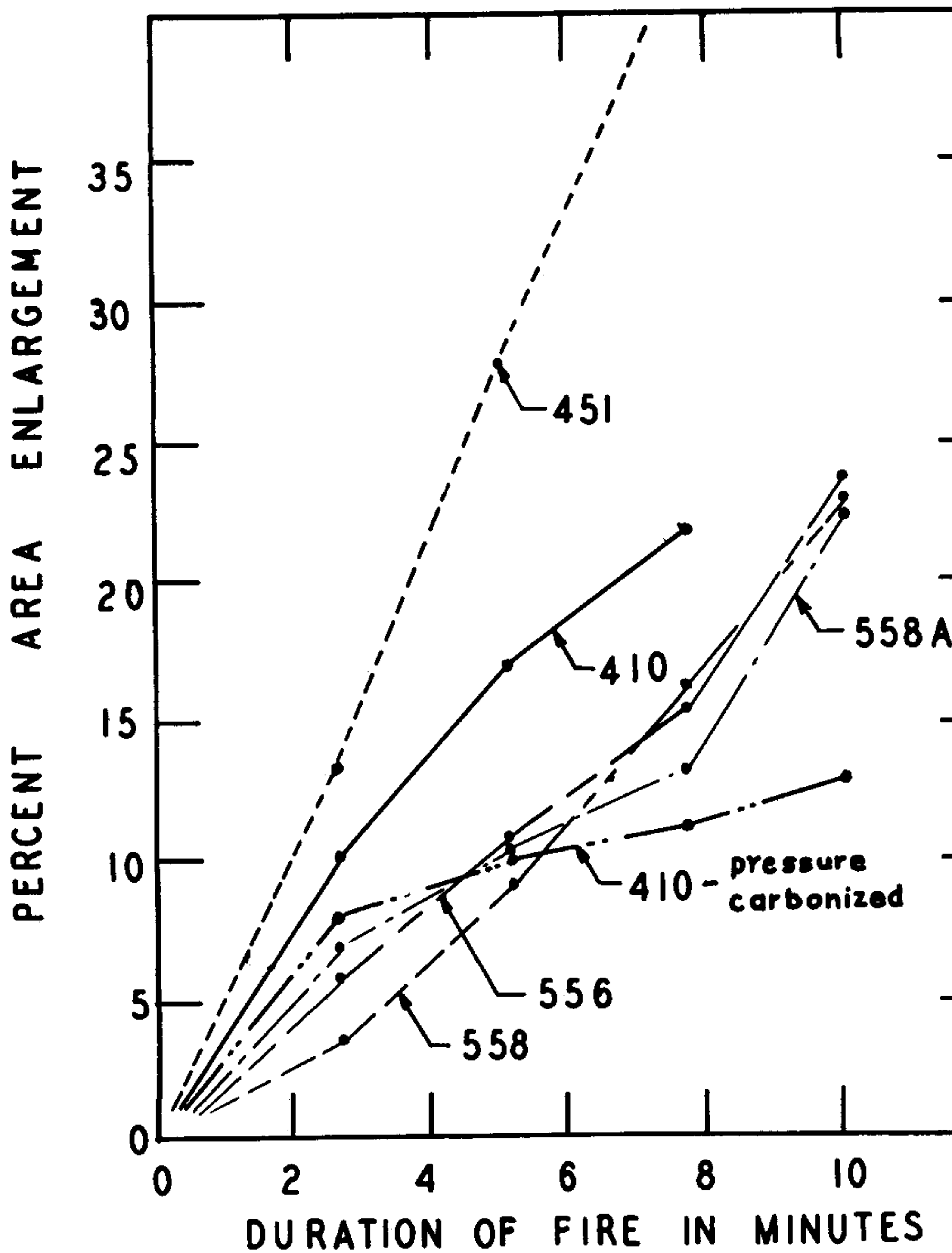

FIG 4

Percent Area Enlargement

its solidification temperature, the vacuum was released and the sample removed from the melt. This process impregnated the sample and prevented the silicon carbide from pulling out.

A greater contrast between the graphite and the matrix was obtained by oxidation of the graphite with fuming nitric acid and potassium chlorate.

III DISCUSSION OF RESULTS

From Fig. 4 it is evident that composition 451 enlarged more rapidly in the XMRM-2 test than the original Alfred. The change in the SiC to graphite ratio from 3:1 to 1:1 was in itself not beneficial.

Compositions 556, 558 and 558A exhibited about the same resistance to high temperature flame erosion and from this it was concluded that the larger grained SiC contributed to the erosion resistance of the material.

It was also evident that the more dense, pressure-carbonized 410 was significantly more erosion resistant than the cold pressed, carbonized 410, and in fact, was slightly better in repeated bursts, than the improved compositions.

Had there been time to pressure-carbonize composition 558 and 558A even better erosion resistance might have been obtained. These investigations of composition and pressure-carbonization were conducted concurrently and there was insufficient time available to use the results of the composition study in the pressure-carbonization work.

IV FABRICATION OF 1000 LB. THRUST NOZZLES

One nozzle was produced using Alfred 410 and the original cold tamping process followed by slow carbonization to 1830°F packed in graphite. This nozzle was submitted to WADC for evaluation for two purposes: (1) to compare the present motor conditions with those of several years ago when a large number of Alfred 410 nozzles were tested; (2) to constitute a basis for comparison of improvements in composition and forming techniques developed under the present contract.

Compositions 556 and 558 were selected on the basis of the XMRM-2 tests for submission in full scale nozzle forms. Three nozzles of composition 556 and two of 558 were cold tamped and carbonized by the old process. Actual glaze firing at high temperatures was found unnecessary in the case of Alfred 410 because the glaze developed in the rocket test. However, as a check, one of the two composition 556 nozzles was glaze fired at 3100°F for thirty minutes.

Two nozzles of Alfred 410 were fabricated by the pressure carbonization method using a split ring stainless steel die and employing the following process:

(1) The mixed material, heated approximately to 212°F was tamped into a heated stainless steel split ring mold. Fig. 5 shows the cross section view of the mold, while Fig. 6 shows the mold assembly ready to be heated.

(2) The mold was placed in the furnace and heated at the rate of 90°F per hour to 1100°F under a constant pressure of 3500 psi.

(3) Pressure was removed at 1100°F and the furnace allowed to cool to 750°F. At this temperature, the mold was taken out of the furnace, disassembled, and the nozzle removed. Hot stripping of the die eliminated cracks thought to be the result of the differential contraction of the die and part. The nozzle was then refired, packed in graphite flake, to 1832°F to assure that all volatiles were removed.

These nozzles were all shipped to the Materials Laboratory, WADC for evaluation. The results of this evaluation may not be available for several months.

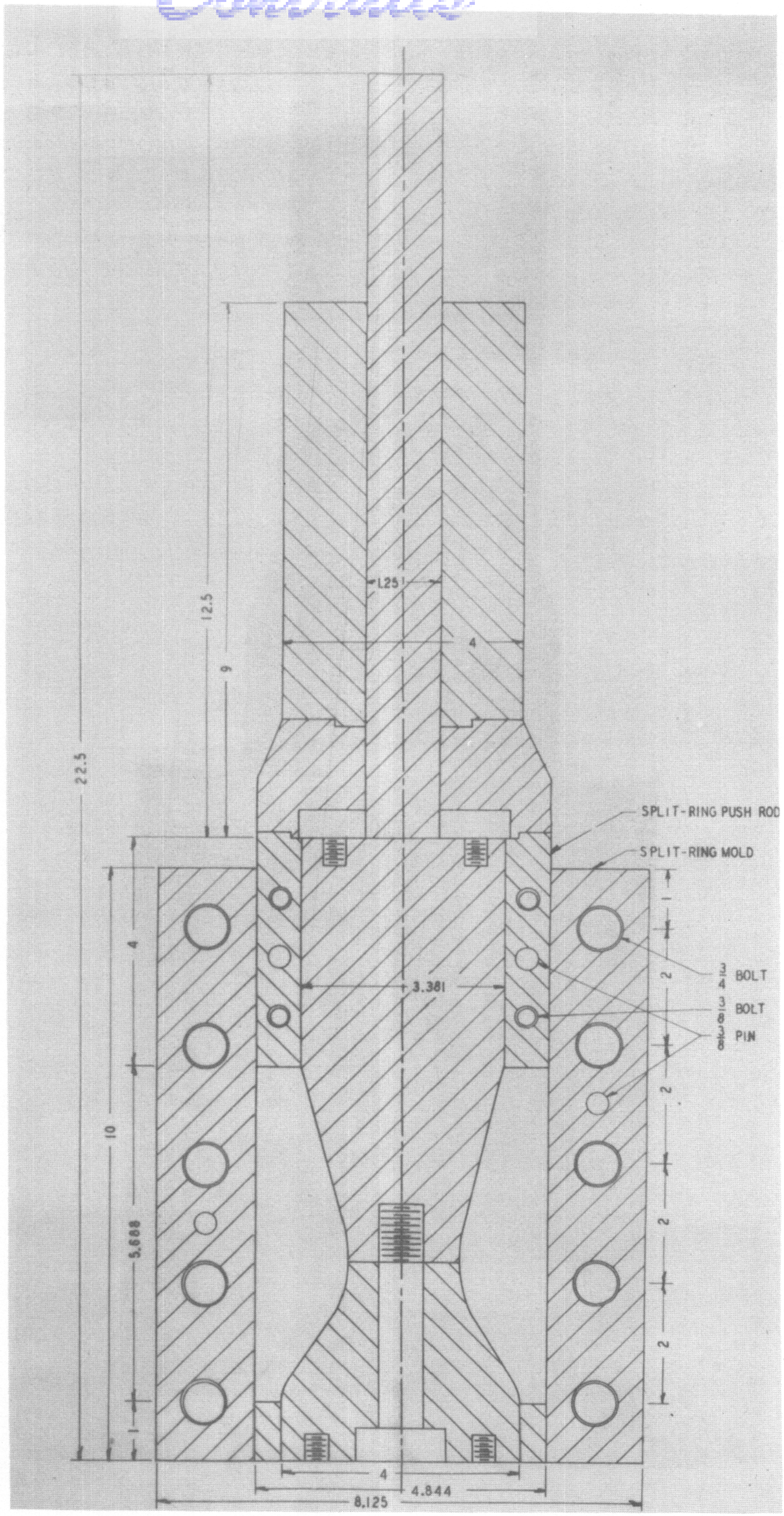

Fig. 5

Hot Press Carbonization Die - 1000 Lb. Nozzle

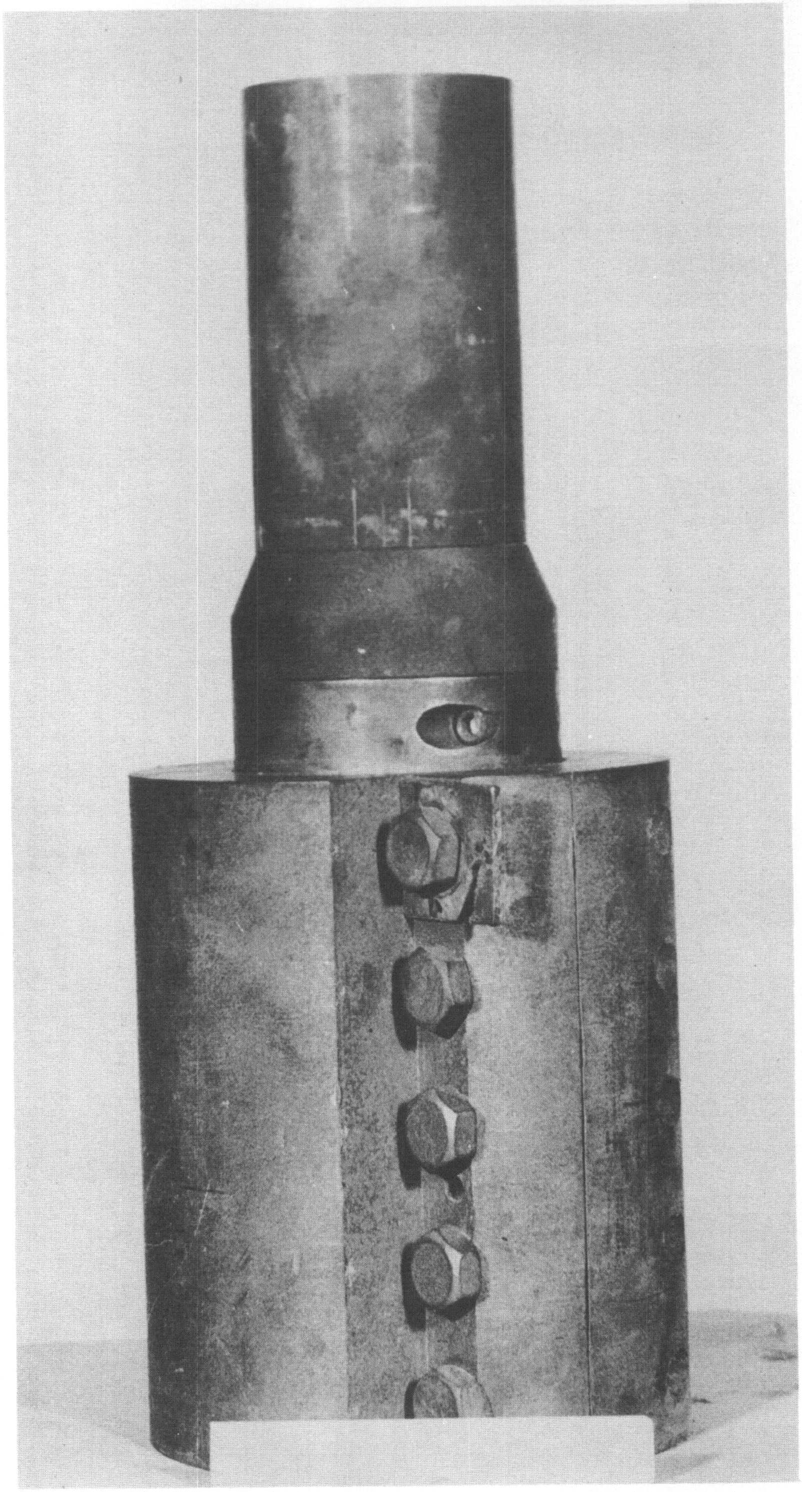

Fig. 6

1000 Lb. Nozzle Mold - Ready to be Heated

V SUMMARY OF CONCLUSIONS

(1) Alfred 410 may be improved in resistance to high temperature flame erosion by the substitution of large grained SiC for "settling tank fines" SiC.

(2) The resistance of pressure-carbonized carbon bonded SiC-Graphite was shown to be superior to that produced by the cold tamping-carbonization process.

(3) The density of carbon bonded SiC-Graphite was improved by 15% and the porosity reduced by 40% by use of pressure-carbonization.

(4) Several technical-engineering problems were overcome in the development of a method for the pressure-carbonization of carbon bonded SiC-Graphite and the process was shown to be practical.