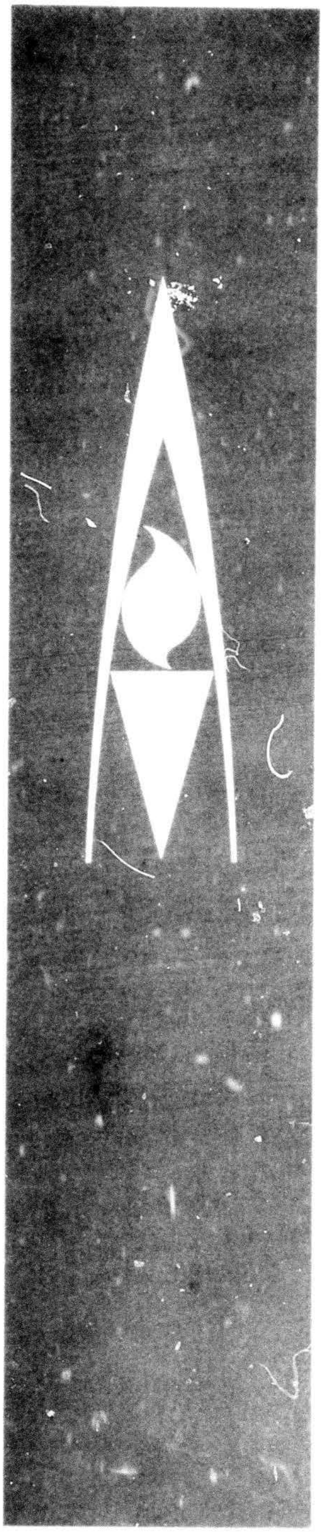

BEHAVIOR OF NOZZLE MATERIALS UNDER EXTREME ROCKET MOTOR ENVIRONMENTS

Contract NOw 64-0393-c

First Quarterly Progress Report

August 1964

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CORPORATION

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August 31, 1964

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Bureau of Naval Weapons
Washington, D. C. 20360

Attention: RMMP-23 (Mr. Sol Matesky)

Subject: Contract NOw 64-0393-c

Gentlemen:

Attached is the First Quarterly Progress Report on the subject contract. This report covers the months of June, July, and August 1964.

Distribution of this report is being made to the CPIA distribution in accordance with your instructions as shown in the back of this report.

Very truly yours,

ATLANTIC RESEARCH CORPORATION

James D Batchelor

James D. Batchelor
Project Director

JDB:khm

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ALEXANDRIA VIRGINIA

BEHAVIOR OF NOZZLE MATERIALS UNDER EXTREME ROCKET MOTOR ENVIRONMENTS

Contracy NOw 64-0393-c
First Quarterly Progress Report

Submitted to: Bureau of Naval Weapons
Department of the Navy

Submitted by: Atlantic Research Corporation
Alexandria, Virginia

Period Covered: May through July 1964

Contributors: J. D. Batchelor
J. B. Murphy
E. L. Olcott

August 1964

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1.0 INTRODUCTION

The current program has as its objective a research investigation of the behavior of rocket nozzle materials under extreme rocket motor environments. The environments of particular interest are those associated with uncooled nozzle service in advanced or future solid propellant rocket motors. Principal emphasis is to be placed on graphitic materials, high-melting carbides, and the most refractory metals. Chemical reactions effects of the propellant exhaust environment on these materials are to be studied as well as thermal and mechanical factors. Methods of reducing or controlling deleterious effects are also of interest.

This report is the First Quarterly Progress Report and it covers the period from May 1 through July 31, 1964.

2.0 SUMMARY

During the first quarterly period of the program, work was carried out on two experimental techniques, and preliminary results were obtained on two different materials. A plasma torch test technique which exposes the bore of a tubular specimen to a high heat flux and a high velocity of selected gas mixtures was conceived and developed. The necessary hardware was designed and constructed. The technique was proved satisfactory in tests of Graphitite-G grade of graphite with nitrogen, hydrogen, and carbon dioxide. The applicability of the tubular specimen geometry to refractory carbides was indicated by tests with NbC cylinders backed up with a graphite-carbide matrix. The equipment for the plasma torch impingement test method was renovated. A number of graphite specimens were machined for future use in this equipment.

3.0 EXPERIMENTAL PROGRAM

The primary method of providing rapid heating and exposing specimens to various reactive gases involves the 80-Kw plasma torch. In previous work, considerable success was achieved in tests in which the plasma torch flame was impinged on the frontal area of a hemispherical specimen mounted within a protective shroud tube which prevented exposure of the specimen to the air. This technique is to be used in part of the work in this program. However, a search was also made for other exposure techniques which might better simulate the flow geometry of a rocket mozzle, provide simpler tests, provide more uniform exposure conditions, or in some other way provide additional useful data. The most promising technique found was the exposure of tubular specimens to the flow of hot gases issuing from the plasma torch directly through the bore of the test specimen. To date on this program, these two experimental procedures, using flow through tubular specimens and impingement on hemispherical specimens, are the only techniques which have been investigated. The results during the first quarter are discussed separately according to the experimental technique used.

3.1 Plasma Torch Tests of Tubular Specimens

A procedure to test tubular specimens with the plasma torch was devised during the current report period. The equipment used for this procedure was intentionally kept as simple as possible. The initial design of test hardware utilizes a thick-walled sleeve of baked carbon as an insulator between the tubular specimen and the steel housing Water cooling was intentionally avoided to reduce the heat losses to a minimum. A cross-section of the test section is shown in Figure 3-1.

For reaction tests, the test section was attached directly to the front of the plasma torch which was equipped with a mixing nozzle. Thus, the hot plasma gas from the torch was first blended with the reactive gas in the mixing chamber and then the mixture passed directly

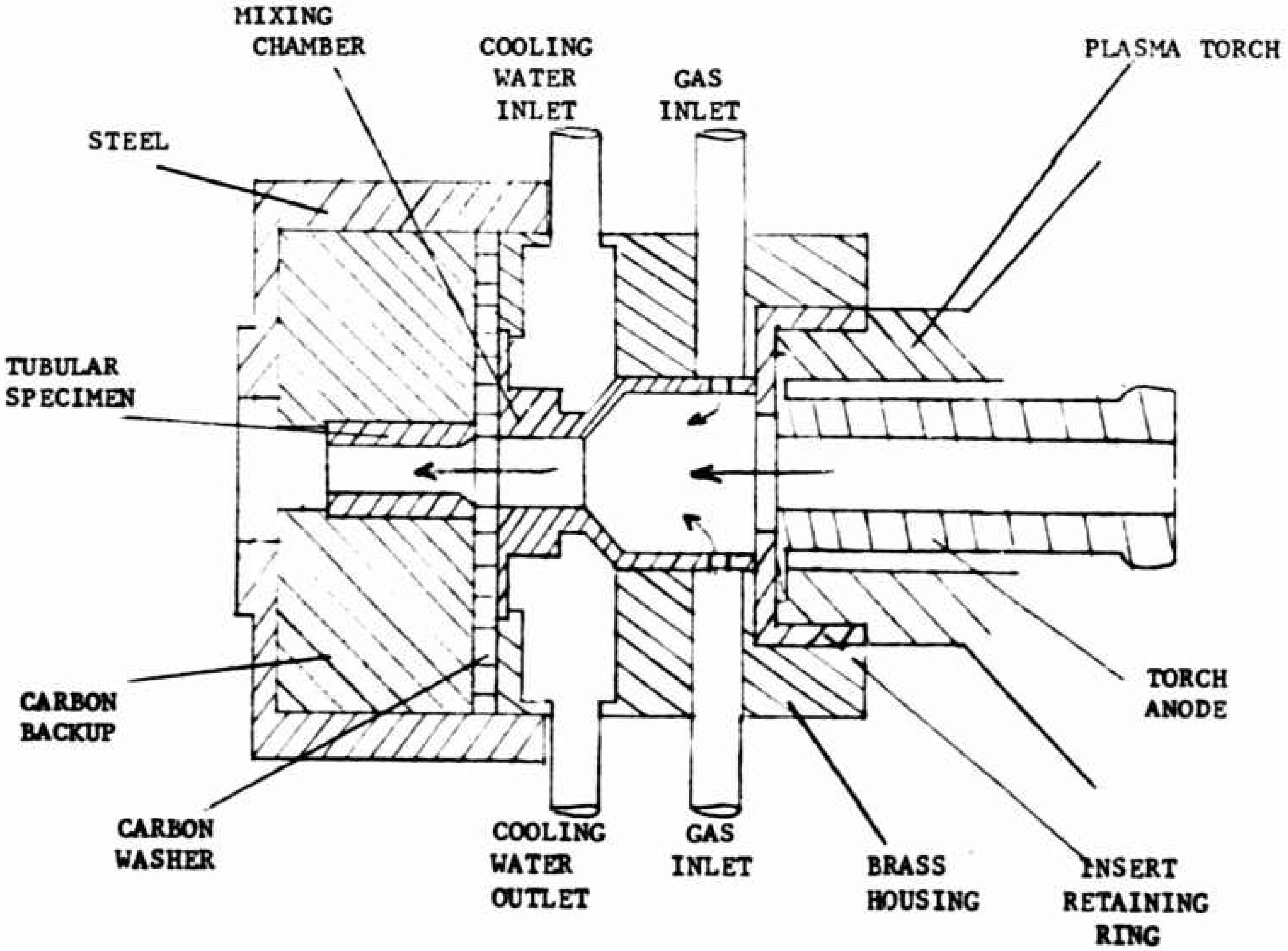

Figure 3.1 Cross-Section of Equipment for Plasma Torch Test of Tubular Specimens.

through the bore of the tubular specimen. Because of the insulating back-up behind the specimen and the high heat flux to the exposed surface, the temperature along the bore increases rapidly to a reasonably constant value. In the initial work , the feasibility of this test method and the suitability of the test fixture were the principal factors investigated. No measurement of the actual temperature of the exposed surface was attempted; rather, all tests were carried out at a single input power setting of the plasma torch.

3.1.1 Graphite Specimens

A series of tests was carried out using tubular specimens 1/2 inch in outside diameter, 1/4 inch in inside diameter and 3/4 inch in length, machined from extruded rod of Graphitite G, a premium grade of graphite from Basic Carbon. Each test was run using a standard torch operating condition of 500 ampere current and 200 SCFH of nitrogen as the primary plasma gas.

The erosive effect of the nitrogen plasma gas on Graphitite G in the test confuguration was investigated first. Tests of several duration were run with the following results.

Duration of Exposure	Wt. Loss Total (gm)	Wt. Loss Rate (gm/sec)	Radial Erosion Total (mil)	Radial Erosion Rate (mil/sec)
15	0.0103	0.0007	0	0
15	0.0098	0.0007	0	0
55	0.1027	0.0019	1.5	0.03
90	0.1094	0.0012	1.0	0.01

The increase in the bore of the test specimens was very small throughout most of the length. A very obvious loss of material occurred at the downstream edge of the specimen. This loss, which appears to be related directly to the flow effects caused by the sudden expansion at the exit end of the tubular specimen, largely accounts for the observed weight loss. The weight loss rate was not constant as shown by the runs of different durations. It is logical that during very early time the loss rate is low before the specimen is well heated. Much later, after significant rounding of the exit edge occurs, the loss rate should drop again. The results are in agreement with these predictions. The tests of 15-second duration were made specifically to provide a weight loss correction for chemical reaction tests. The preheat period used in all reaction tests consisted of 15-second exposure to the primary nitrogen plasma gas alone. Thus, the weight loss which occurred prior to the introduction of the reactive gas component is that found in the short tests listed above. A correction of approximately 0.010 gram can be made to cover the effect of the preheat period.

Two tests were carried out with the addition of hydrogen to the nitrogen plasma gas. These tests were made for two reasons. First, hydrogen can react directly with graphite to produce gaseous products; thus, the reactivity of hydrogen with Graphitite G specimens under our test conditions is of interest. Second, the grade of nitrogen used as the primary plasma gas in all tests contains up to one percent hydrogen added to the cylinder gas as a step in the removal of trace oxygen. Thus, it was also of interest to see if the reactivity of hydrogen had any significant role in the weight losses observed in the tests with the nitrogen plasma tests. The results of the hydrogen reaction tests were as follows.

Duration of Exposure	H_2 Concentration (percent)	Weight Loss		Radial Erosion Rate (mil/sec)
		Total	Corrected	
30 second (+15 sec N_2 preheat)	3.8	0.0737	0.0727	0.02
30 second (+15 sec N_2 preheat)	7.4	0.0713	0.0703	0.05

Conclusions which can be drawn from these results include the fact that at the surface temperature reached under the experimental conditions, the reactivity of hydrogen with Graphitite G is negligible because no significant radial erosion occurred. This, of course, will not hold true at much higher temperature levels. The distinct weight loss observed indicates that significant material removal occurred from thermal and mechanical effects. Again, this loss was localized at the downstream edge of the specimen. The magnitude of the losses is similar with the expectations for nitrogen plasma gas only, although tests of exactly the same total duration were not made.

Following the initial tests with the less reactive gases discussed above, a more extensive series of tests was made using CO_2 as the reactive gas. In the first group of tests, the reproducibility of the erosion observed with CO_2 additions to the plasma gas and the effect of the quantity of CO_2 added were observed. In each of the six tests made, the specimen was preheated by a 15-second exposure to the nitrogen plasma (500-ampere arc current, 200-SCFH nitrogen flow rate). Following preheat, the selected CO_2 flow rate was added through the mixing chamber for a 30-second reaction period. During the cool-down period, nitrogen at ambient temperature was passed through the bore of the specimen. The results of these tests are summarized below. The weight losses reported are corrected for the loss observed during 15-second exposure to the nitrogen plasma since this loss is not associated with the CO_2 exposure. A significant axial variation in erosion rate was noted and to illustrate this, average erosion rates are reported for three locations, near the inlet, at the center, and near the exit of the tubular section of the specimen.

CO_2 Flow Rate	Corrected Weight Loss	Average Specimen Erosion Rate, mil/sec		
		Inlet	Center	Exit
(SCFH)	(gm)			
50	0.614	0.95	0.70	0.40
50	0.611	0.90	0.63	0.43
50*	0.568	0.88	0.55	0.38
100	0.474	0.77	0.45	0.28
100	0.451	0.68	0.45	0.32
75	0.522	0.80	0.53	0.35

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* Specimen reversed (i.e., tapered edge, downstream)

Several interesting facts are apparent from examination of these data. The reproducibility of duplicate tests is reasonably good. The weight losses vary less than 2 per cent from the mean. The erosion rates vary somewhat more (up to 6 to 7 per cent) from their mean in duplicate tests.

The most peculiar result of these tests was that an increase in the flow rate of CO_2 from 50 to 100 SCFH caused a decrease in the extent of reaction. This behavior seems peculiar because the CO_2 concentration increases with CO_2 rate from 20 per cent to 33 per cent. On the other hand, the addition of the CO_2 has a cooling effect on the plasma gas which increases with higher rates of addition. It is apparent that the temperature effect is controlling under the test conditions used. In one sense, this is encouraging since it indicates that the surface reaction rate is involved in the observed extent of reaction and that the results are not limited solely by diffusion considerations.

Fortunately, a straightforward method was available to separate to a large extent this interaction between CO_2 concentration and the temperature of the gas mixture. Instead of varying the ratio of hot plasma gas to cold secondary gas to achieve different CO_2 concentrations, the simple alternative of holding the hot to cold gas ratio constant while varying the concentration of CO_2 in the cold gas was used. In actual practice, a mixture of CO_2 and nitrogen was added at a fixed rate to the hot nitrogen plasma so that the cooling effect was held essentially constant. By increasing the fraction of CO_2 in the CO_2-N_2 mixture, the concentration of the CO_2 in the hot reactive mixture was increased. Using this technique, a series of tests was carried out to measure the effect of CO_2 concentration on the erosion rate of Graphitite-G tubular specimens. In each test (with one exception noted in the table) the cold gas addition to the hot plasma gas was at the rate of 50 SCFH. The hot plasma flow was generated in the same way as in previous tests, namely 200-SCFH nitrogen flow and 500-ampere arc current. The results of these tests are summarized in the following table. The data for the highest concentration of CO_2 is taken as the average of the two reproducibility tests reported above since those tests were also made with 200 SCFH of hot plasma nitrogen and 50 SCFH added cold gas. Exposures in each test again consisted of 15 seconds preheat in nitrogen and 30 seconds of reactive gas flow.

CO_2 Concentration (per cent)	Corrected Weight Loss (gram)	Erosion Rate (mil/sec) Inlet	Center	Exit
20	0.612	0.92	.66	.42
16	.497	0.75	.55	.38
10	.502	0.67	.50	.40
5.3*	.392	0.52	.43	.28
4	.375	0.47	.32	.28

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* Total cold gas rate only 37.5 SCFH in this test.

These data show a much more consistent trend of increased reaction with increased CO_2 concentration than the earlier tests in which the total quantity of cold gas addition was varied from test to test. The data for the 16 per cent CO_2 concentration appear to be in error on the low side (especially the weight loss) but it was assumed, for the time being at least, that this was simply an experimental aberration. The general trend of both the weight loss and erosion rate data is a rapid rise in reaction at low CO_2 concentrations with a leveling off at the higher CO_2 concentrations. This is reasonable behavior. Based on these tests, it was judged that a suitable general procedure has been developed. Future tests will utilize essentially the technique described for this work with CO_2.

3.1.2 Refractory Carbide Specimens

Another class of materials which are of interest in this study in addition to graphitic materials are the refractory carbides. To determine the applicability of the tubular specimen test technique to refractory carbide materials, the Carborundum Company was contacted concerning the tubular specimens. Carborundum provided four specimens each of TaC, NbC, HfC, and ZrC. The configuration of these specimens was the same overall (i.e. 1/2" o.d. × 1/4" i.d. × 3/4" long) as the graphite specimens. A composite construction was used in which the inner 40 per cent or so of the wall was pure carbide and the outer portion was a 70 per cent graphite-30 per cent carbide mixture. This lower modulus back-up material concept has been successfully applied to nozzle insert fabrication by Carborundum.

During the period of this report, feasibility testing was carried out with one of the carbides. Because of the thermal shock sensitivity characteristic of the refractory carbides, proof was required that such tubular specimens could withstand the thermal cycle involved in the plasma torch test procedure. Two of the NbC specimens were tested with CO_2 exposures. The usual 15-second preheat in the nitrogen plasma was followed by exposure to an 11-per cent concentration of CO_2. The data from these tests are shown below.

Reaction Period (sec)	Specimen Weight Loss (gram)	Specimen Erosion Rate, mil/sec.		
		Inlet	Center	Exit
20	0.490	0.65	0.28	0.05
30	1.017	0.65	0.32	0.12

The results are significant. The carbide specimens did not appear to be damaged by the thermal cycle. Detailed examination for cracks has not been carried out. The chemical corrosion of the carbide was very significant. A high melting-point product (presumably, the oxide) was apparent as beads at the sample exit in the first test. In the second test, a spike actually grew out of the end of the specimen during cool-down. It is likely that this was formed from molten oxide which blew out and rapidly solidified when the test was terminated and the nitrogen cooling flow established. The main significance of these tests, however, was the fact that no massive break-up or ejection of the carbide was observed.

3.2 Plasma Torch Impingement Tests

The test procedure in which the plasma flame impinges upon the face of a hemispherical specimen was used extensively in the earlier program of reaction studies. During the current quarter, no further tests were performed with this technique, but a supply of Graphitite-G specimens were machined and the protective shroud equipment in which impingement tests are performed was renovated. An improvement was made in the rigidity of the inlet flange of the protective shroud and a new set of quartz windows was obtained. Tests of both Graphitite G and pyrolytic graphite will be the first scheduled in this unit in the coming quarter.

4.0 FUTURE WORK

Additional reaction tests will be made using both the tubular specimen configuration and the impingement configuration with the plasma torch. The tubular specimen test procedure, which is new to this program, was successfully developed and proved suitable for both graphite and refractory carbide specimens. The particular procedure worked out for one grade of graphite will be applied to additional specimens in gases other than CO_2, to specimens of other graphites, and to additional specimens of carbides. Temperature instrumentation will be added and a suitable procedure to estimate the specimen surface temperature will be sought. The impingement test procedure will be activated for an extension of the data obtained in our previous program.

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