First Quarterly Progress Report

Covering the Period 1 July 1969-30 September 1969

DEVELOPMENT OF HIGH TEMPERATURE MATERIALS FOR SOLID PROPELLANT ROCKET NOZZLE APPLICATIONS

NGR 34-002-108

For

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By

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INTRODUCTION

National Aeronautics and Space Administration research grant NGR 34-002-108 was awarded to North Carolina State University for the development of materials for use in solid propellant rocket nozzles. The materials to be developed are to be resistant to both mechanical and chemical erosion as well as resistant to thermal shock. The materials should have the ability to provide the above properties particularly in the rocket nozzle throat area where the environment is most hostile.

Recent research has failed to provide a satisfactory material because one or more of the above properties. Graphites have been widely used but chemical erosion has harmed their performance at high temperatures. Refractory metals and their alloys have shown promise but without regenerative cooling, their melting point is too low. Ceramic materials also have shown promise but they are plagued by lack of resistance to thermal shock and abrasion.

This investigation proposed to develop a composite of refractory metals and/or graphite with a ceramic base. By the formulation of such a composite it is felt that best properties of each type of material used may be imparted to the composite so that it may have the mechanical and chemical erosion and thermal shock properties required for solid propellant rocket motor nozzles.

The first quarter of the research period has been used for necessary preliminary work. This work is itemized below and is discussed later:

1. Acquisition of information on equipment and supplies

2. Selection and acquisition of equipment and supplies

3. Design and construction of custom equipment

4. Installation of equipment

5. Continuation of literature survey

6. Formulation tests

ACQUISITION OF INFORMATION ON EQUIPMENT AND SUPPLIES

After receipt of the grant, information was obtained on the necessary equipment and supplies. Initial needs dictated contact on plasma generator unit, control unit, gun, nozzles, gases, and powder feeders; the necessary carbides, oxides, nitrides and borides; graphites; tungsten base alloys; and other miscellaneous equipment and supplies.

Equipment and supplies were subsequently purchased from this information.

SELECTION AND ACQUISITION OF EQUIPMENT AND SUPPLIES

A Thermal Dynamics Model TD HVA-40 power unit, 50 N control unit and F40 torch has been acquired as the basic plasma unit which is shown in figure 1. Nozzles, mixing units, and powder feeds are presently being ordered.

Poco graphites of various grades are to be used and grades AXF-5Q, AXF-9Q, AXF-Q1, HPD-1, and CZR-1 have been acquired. Wah Chang was the supplier for HFC, HFO, and ZrC. Cerac Y_2O_3 is to be used. General Electric tungsten and tungsten -3% rhenium wire and plate was purchased.

Gases, regulators, furnace tubes, thermocouples, and other assorted equipment and supplies were obtained locally as required.

DESIGN AND CONSTRUCTION OF EQUIPMENT

Design of new custom equipment and redesign of existing of equipment for use in this investigation has been and is continuing to be done. An existing hot process is being fitted with a larger vacuum system and a linearly variable differential transducer-type extensionmeter is being built to measure the hot press die travel during firing. A sample holder and torch heat shield is being designed for use in dynamic oxidation and erosion testing with the plasma unit.

The hot press has been fitted with an induction heating unit which will obtain firing temperatures of approximately 5000°F and will accept samples up to 0.75 inches in diameter. The six inch diffusion pump coupled with a 50 cubic feet per minute mechanical pump will produce chamber pressures in the 10^{-5} torr range and should provide ample oxidation protection during the firing process.

The linearly variable differential transducer-type extensionmeter is being developed to measure die displacement vs. times for mass transport analysis during firing. The radiant should provide information on maximum densities obtainable under the pressing conditions.

The sample holder is being designed to be used with both cylinder type samples and block samples. The unit provides a heat proofed stand for the sample and a shield for the plasma torch. Figure 4 illustrates the basic unit.

An oxidation resistance test chamber has been designed and constructed. The chamber illustrated in figure 3 is essentially a mullite tube which is fitted with a sample holder and a gas flowmeter and is heated in a tube furnace.

INSTALLATION OF EQUIPMENT

The recently acquired plasma unit has been installed and is in satisfactory operating condition. The hot press equipment is installed and is in the process of a shake down. The work on the linearly variable differential transducer-type extensionmeter is nearing completion and should be totally functional by the time the hot press is in satisfactory operating condition. The oxidation resistance test chamber is installed and is ready for testing. All other existing equipment is in satisfactory operation condition.

Within a period of a week all equipment should be in a condition such that all necessary testing may be performed.

CONTINUATION OF LITERATURE SURVEY

The literature survey is being continued as more specific information is needed. The survey is somewhat hampered because to the best of our present knowledge no one has investigated the proposed composites under the conditions encountered in solid propellant rocket motor nozzles.

FORMULATION OF TESTS

After a survey of the literature, a group of tests which would be necessary for the evaluation of the composites and the input materials were established. This group of test which is discussed below is considered a minimum requirement and may be amended during the course of the investigation.

Because oxidation is considered a major problem, a test was devised to test both input materials and composites. In oxidation resistance testing, type of atmosphere, surface area to volume ratios (geometric configuration), temperature, atmosphere flow rate, and time are considered to be the major variables of the test. In the low temperature oxidation test, it was decided to hold constant the surface area to volume ratio (or geometric configuration) of the sample, the temperature of the environment, the atmospheric flow rate, and the time. The type of material and the atmosphere are independent variables and the change in weight is then a relative measure of oxidation resistance.

The oxidation resistance test may be performed in two ways: subjecting the material to a plasma flame to which an oxidizing gas has been added or subjecting the material to a shower moving environment of oxidizing gases at a necessarily lower temperature. Because of the high velocity of gas in the plasma flame and its erosion effect it is felt that the second method is a better measure of the oxidation of the materials under investigation. This test is to be done in the oxidation resistance test chamber described in the section under Design of Equipment. Atmospheres of 80% Ni-20% O_2, 100% O_2, and 100% CO_2 are to be used.

Thermal shock testing will be of a more conventional method. The materials will be cycled between a nitrogen plasma flame and room temperature for specified time intervals until fracture occurs. The number of cycles to failure will be used as an index of thermal shock resistance. Because the porosity of ceramic based materials may be related to the thermal shock resistance, the effect of porosity of the ceramic base materials will be investigated. The plasma equipment to be used is described in the section on Selection and Acquisition of Equipment and Supplies.

The applicability of the composite materials to solid propellant rocket motor nozzles will be determined largely by a series of dynamic oxidation and erosion tests which will be accomplished by simulating exhaust gases with plasma equipment. The exhaust gas simulation will be produced by mixing CO_2 and possibly fine Al_2O_3 powder with a nitrogen plasma flame. This gas will be inpenged upon both a flat specimen of each composite and upon a cylinderical specimen with an appropriately machined hole along its central axis. These discs and cylinders will be held by the devices described in the section on Design of Equipment and the plasma equipment to be used is described in the section on Selection and Acquisition of Equipment and Supplies.

Because both carbides and graphite are to be used in the composite materials, it is felt that a check should be made on the embrittlement of the tungsten and tungsten alloys by carbon when exposed to these carbides and graphite. Several mechanical properties of wire exposed to them at elevated temperature will be determined by tensile testing.

The nature of the bonds between the matrix and tungsten and its alloys are not clearly known. To establish the nature of the bond, a sample of each composite will be crushed in compression and a macroscopic and microscopic examination will be made. If deemed necessary, sessile drop wetting studies of matrix materials on tungsten basis may be performed to determine the nature of any chemical bonds.

Physical, chemical, and mechanical properties are to be monitored at all stages of the investigation by a variety of standard techniques. Compatability, phase transformations and stability and phase identification are to be obtained by X-ray diffraction analysis, metallography, and where necessary, electron microprobe and electron microscopic analysis. Tensile and compression testing will be performed as needed.

PROPOSED WORK FOR THE SECOND QUARTER

During the second quarter evaluation of materials and processing techniques will be initiated. This involves the stabilization of oxides with high temperature transformations, development of hot pressing techniques, formulation of binary composites, oxidation testing, thermal shock testing, and an evaluation of phase stability by a variety of techniques previously discussed.

Hafnium oxides is one of the more promising oxides for application in solid propellant rocket engine nozzles. Because it does have a high temperature transformation, it is felt necessary to stabilize the material with yttrium oxide before using it as a base for composites.

Hot processing parameters must be developed for yttrium oxide stabilized hafnium oxide; hafnium carbide; zirconium carbide and combinations of these with graphite and/or tungsten and tungsten -3% rhenium wires (It is proposed, however, that work with ternary composites will be started in the third quarter.)

Evaluation of phase stability during each phase of testing will be accomplished by X-ray diffraction analysis, metallography, and, where necessary electron microprobe analysis and electron microscopic analysis.

Oxidation testing and thermal shock testing of each composite will be performed by previously described techniques.

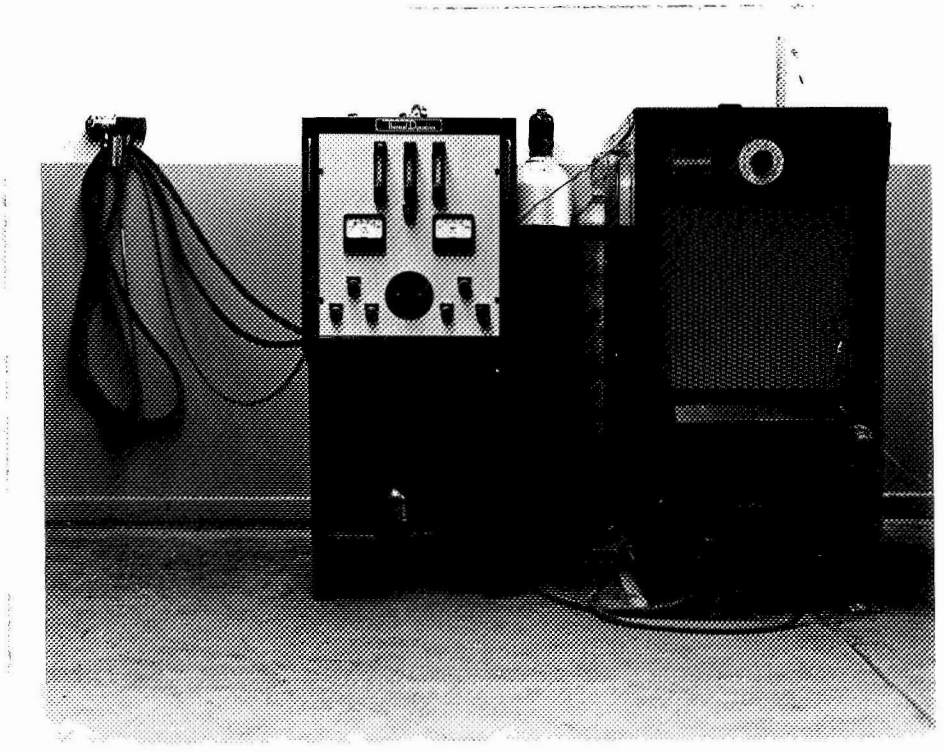
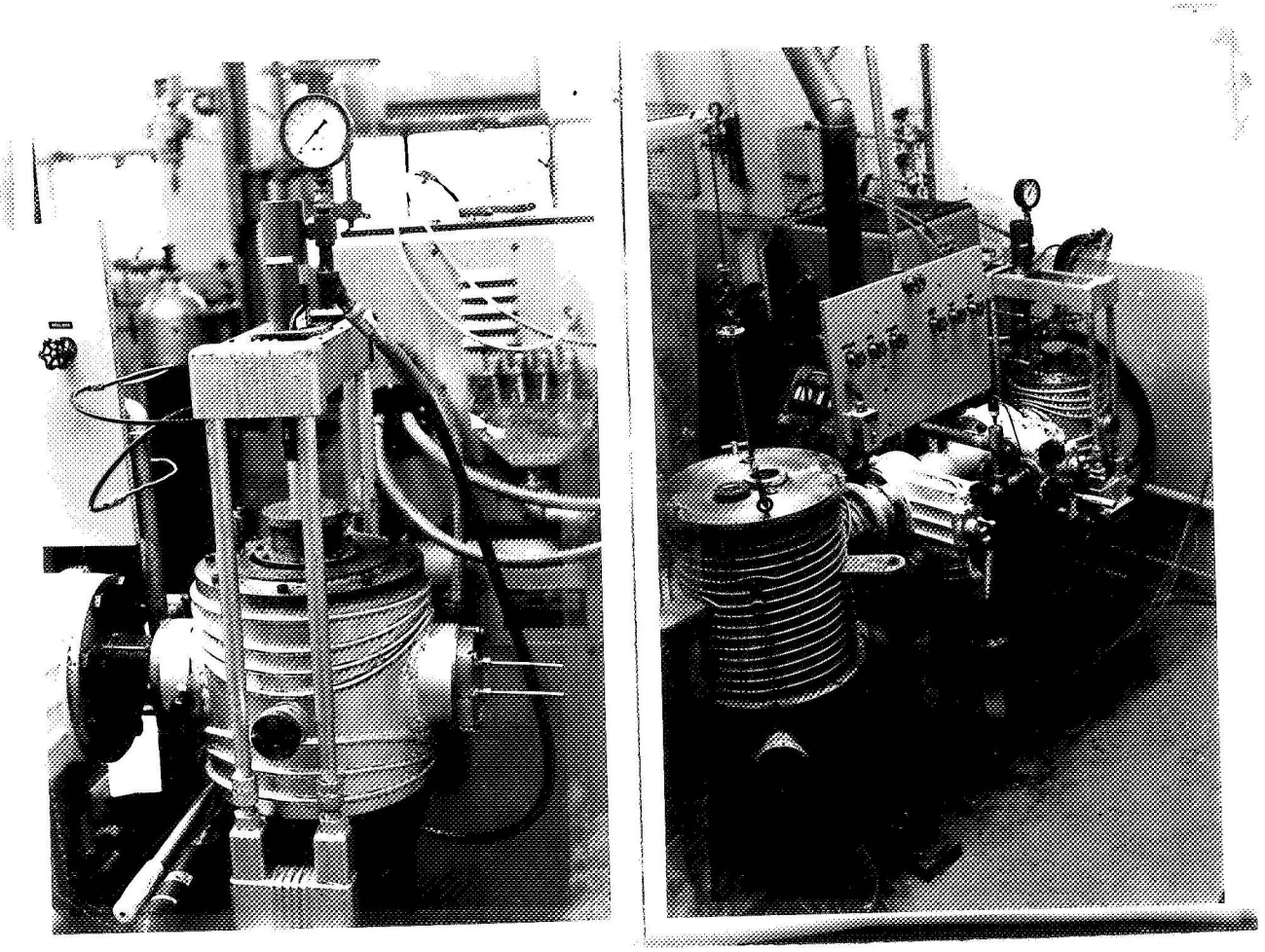


Figure 1. Thermal Dynamics plasma unit installed for dynamic oxidation and erosion testing and thermal shcok testing



(a) (b)

Figure 2. (a) Hot press body
(b) Hot press fitted with 6" diffusion pump and induction heating unit

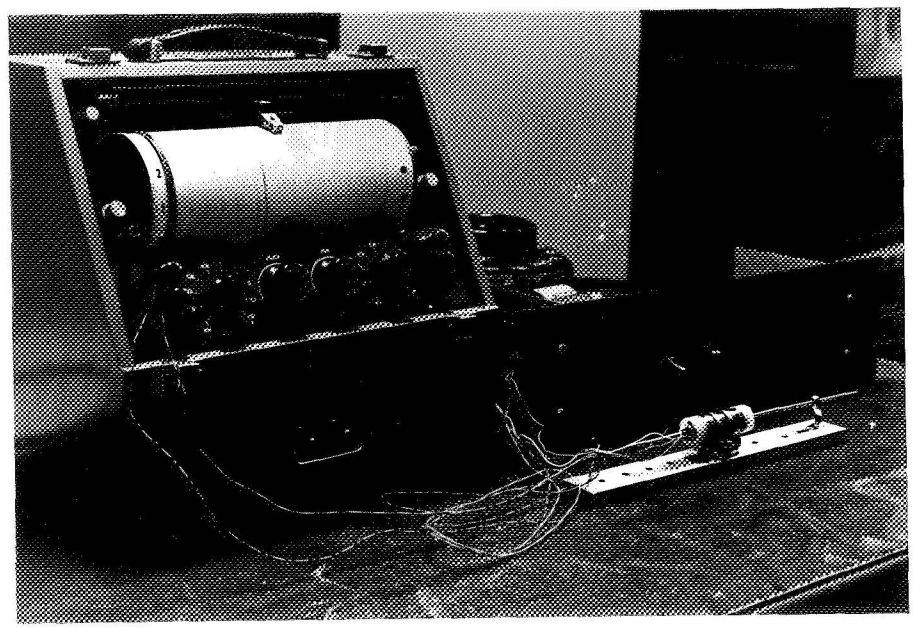
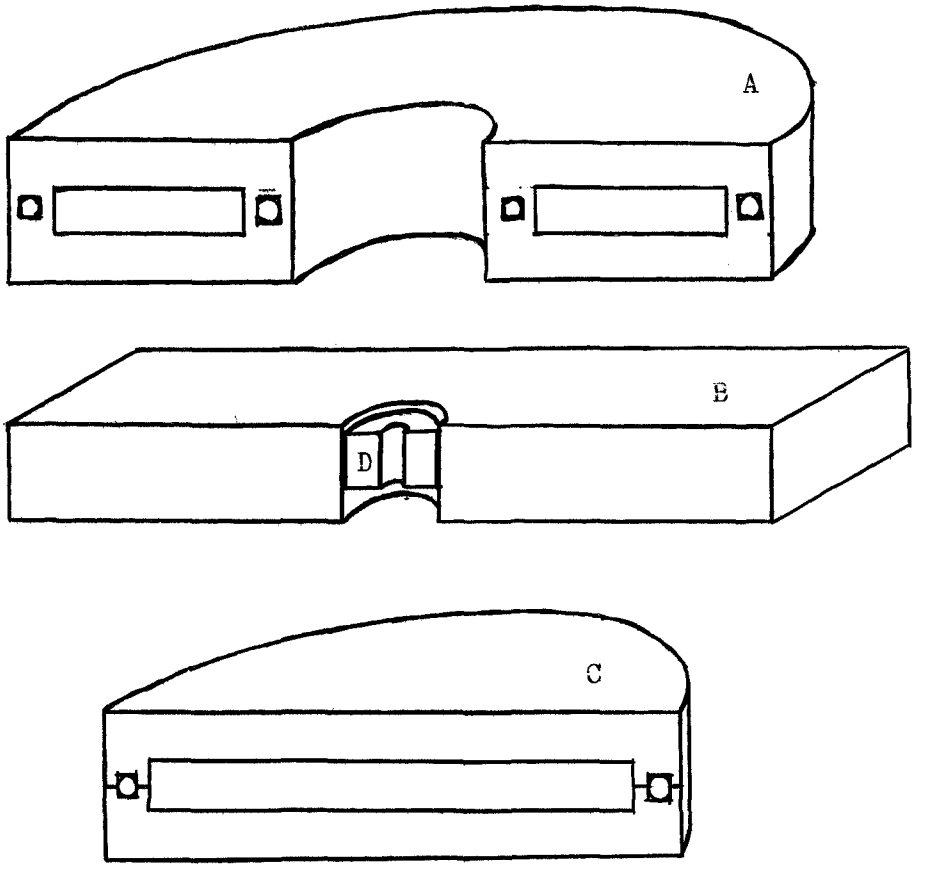


Figure 3. Linear variable differential transducer extensiometer in process of being constructed



A Water cooled copper torch shield
B Pyrolytic graphite sample holder
C Water cooled copper heat dissopater
D Test specimen

Figure 4. Half section schematic of sample holder for dynamic oxidation and erosion testing

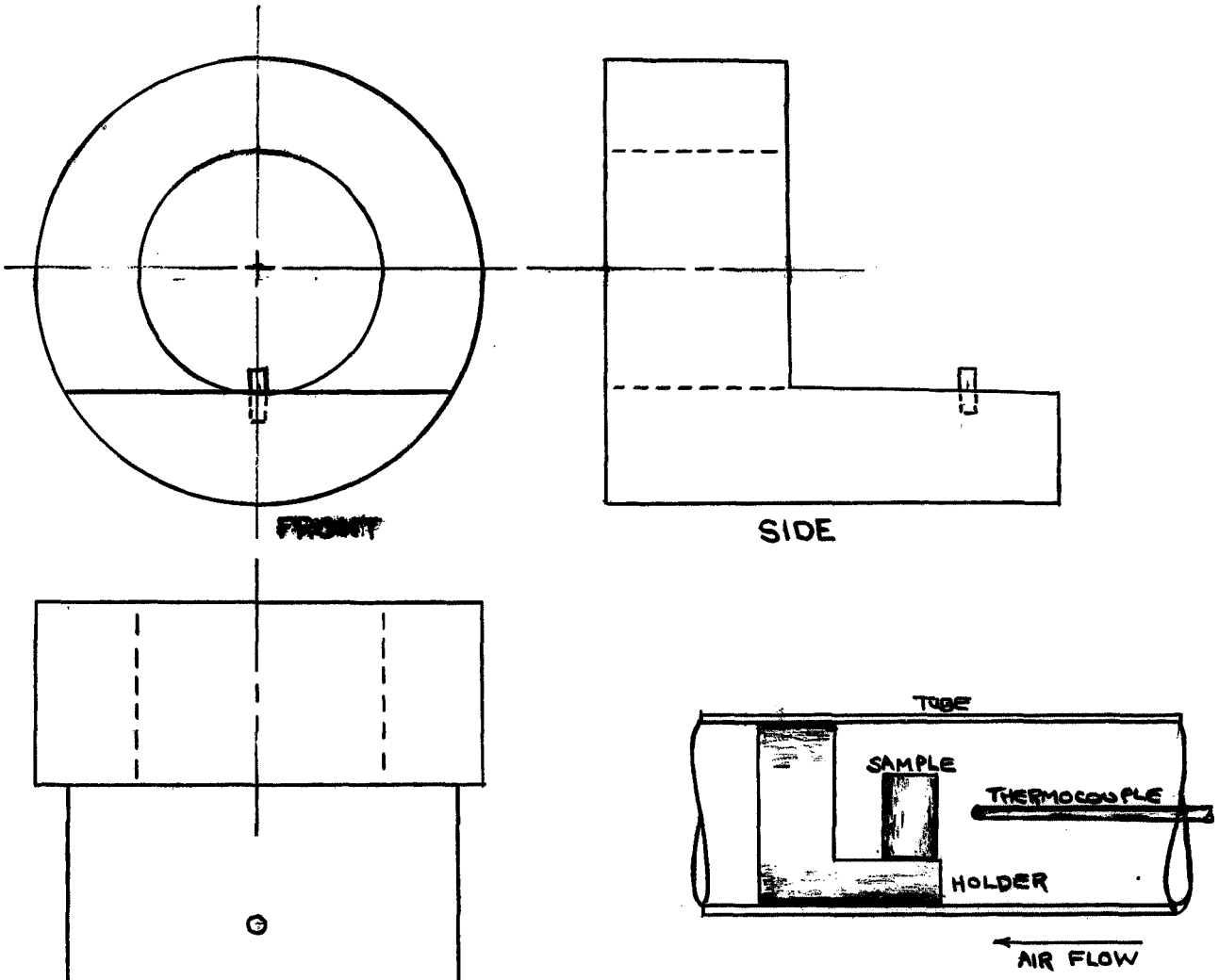


Figure 5. Oxidation resistance test chamber

(a) Top, front, and side views of specimen holder
(b) Position of sample holder, sample, and thermocouple in tube furnace