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REINFORCED OXIDE THROAT INSERT DEVELOPMENT

By
F. T. LALLY and D. P. LAVERTY
TRW Inc.

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Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

**NASA Lewis Research Center
Contract NAS 3-11177
Stephen M. Cohen, Project Manager**

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FINAL REPORT

REINFORCED OXIDE THROAT INSERT DEVELOPMENT

by

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NASA Lewis Research Center
Cleveland, Ohio

Stephen M. Cohen, Project Manager
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ABSTRACT

This program was aimed at developing improved wire-reinforced zirconia nozzle inserts for an $N_2O_4 + 50\% N_2H_4/50\%UDMH$ liquid propellant rocket application. The program studied zirconia matrix materials, refractory metal reinforcing wires, and the variables associated with consolidating these constituents into a composite. Thermal shock tests, other thermal and mechanical tests, and rocket exhaust oxidation studies identified an optimized composite material for fabrication of 3-inch throat diameter inserts. These inserts were evaluated in a rocket engine by a test firing sequence totalling 700 seconds exposure and including several restarts. They performed successfully with no throat erosion and without thermal shock failure.

FOREWORD

This program to develop improved reinforced oxide rocket nozzle throats was carried out during the period July 1967 to December 1968, under Contract NAS 3-11177 by the Materials Laboratory of the Equipment Laboratories Division of TRW. In addition to the personnel associated with this laboratory, several other persons and organizations made major contributions to this program. These include:

Mr. A. G. King of the Zirconium Corporation of America (Zircoa) who directed the development of specialized zirconium compositions and helped interpret the associated test results,

Mr. J. R. Bohn and Mr. C. R. Ernst of TRW Systems who performed the electron-beam thermal shock tests on these materials,

Mr. W. F. Cartwright of TRW Systems who directed the rocket engine exhaust oxidation tests performed at the TRW Capistrano Test Site, and

Mr. J. M. Winter of NASA-Lewis who oversaw the rocket engine test firing evaluation of the nozzles produced in this program.

The contributions to the program that were made by these persons and by several others not specifically mentioned are hereby gratefully acknowledged.

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SUMMARY

A program was carried out with the purpose of developing an improved wire-reinforced zirconia throat insert for use in a rocket engine operating with the $\text{N}_2\text{O}_4 + 50\% \text{N}_2\text{H}_4/50\% \text{UDMH}$ liquid propellant system. This work was motivated by a prior NASA sponsored program of a screening nature which showed the reinforced oxide approach to be effective in withstanding the combined severe oxidation and thermal shock effects of this environment. The scope of the present program was limited to the use of a zirconia matrix material reinforced by randomly dispersed chopped wire of a suitable refractory metal. A five-task program was pursued in this study which culminated in the test firing of nozzles of the best composite developed in this program.

Task 1 consisted of a study of various matrix materials, reinforcing wires, and consolidation procedures for forming the best composites from these constituents. A total of forty-two zirconia-matrix materials were evaluated; these consisted of commercially available materials and of special partially-stabilized zirconia compositions prepared by Zirconium Corporation of America (Zircoa) and by TRW. In general, zirconia partially stabilized to the cubic phase by about 3% MgO proved most successful in this program. A total of eighteen refractory metal wire alloys were evaluated by their retention of strength and ductility after a 4000°F exposure in vacuum, which is typical of composite sintering conditions. A W-3% Re doped lamp-wire alloy proved best for use in further studies. By a study of wire diameters and contents, composites containing from 5 to 10 volume percent of wire in the 2 - 3.5 mil diameter range with a length/diameter (aspect) ratio of about 60 proved to produce the best composites. An isopress-and-vacuum-sintering fabrication approach was determined to be more applicable to these composites than a hot-press procedure.

Task 2 consisted of three types of thermal shock tests used to identify the best composite. For initial matrix material evaluation, a quench test of a disc-type specimen was used. For a more severe test for evaluating composites, a plasma-jet test of a hollow thick-walled cylinder was used. Based largely on this test, the following three composites were chosen for continued evaluation in the program:

- Type A - A matrix of Zircoa's type F410 zirconia reinforced with 5 v/o of 3.5 mil diameter x $3/16''$ long W-3% Re wire.
- Type B - A 2.85% MgO -stabilized medium-texture zirconia matrix reinforced with 5 v/o of 3.5 mil diameter x $3/16''$ long W-3% Re wire.
- Type C - A 2.85% MgO -stabilized fine-texture zirconia matrix reinforced with 7 v/o of 2-mil diameter x $1/8''$ long W-3% Re wire.

Additional thermal shock tests were then performed on hollow cylindrical specimens of these composites using the TRW Systems' electron beam heating technique to obtain a more quantitative evaluation of thermal shock behavior. These tests generally indicated that the Type C material was superior to the others in thermal shock resistance.

Task 3 consisted of tests to determine those thermal and mechanical properties deemed most relevant to rocket nozzle insert application. The Types A, B, and C composites were tested for tensile strength, compressive strength, elastic modulus, thermal conductivity and thermal expansion, all as a function of temperature up to 4000°F or as high as experimental techniques would allow. Wire-matrix bond strength tests were also performed early in the program as part of this task so that a determination of the optimum wire aspect ratio could be made. As a result of these tests, a wire aspect ratio of about 60 was used throughout the program.

Task 4 was comprized of two types of oxidation tests: a rocket engine exhaust test at 4200°F and an air-oxidation test at 3000°F. The rocket engine exhaust test involved placing the composite sample, for times up to 800 seconds, under the exhaust of an operating rocket engine so that a temperature of 4200°F would be reached. The severity of this test allowed a clear-cut discrimination between the overall merit of the Type A, B, and C materials. Type C was clearly the best in this environment and Type A was next best. The air oxidation tests were performed at 3000°F for exposures up to 30 minutes in circulating air. These results allowed an understanding of the oxidation characteristics of this type of material for possible applications other than rocket nozzles.

Task 5 consisted of the design, fabrication, and test firing of nozzle inserts with 3-in. diameter throats. The first nozzle was made of Type C material. It was successfully fired for two 300-second cycles and five 20-second pulses with no throat erosion. The insert retained structural integrity during this test and was removed from the nozzle assembly in one piece for post-test analysis. The second nozzle was of the same dimensional design, but the material was modified by a change in reinforcing wire diameter from 2 mils to 3.5 mils. All other parameters remained the same. This nozzle also withstood the same test firing sequence as the prior one with no net throat erosion. It too was removed in one piece from the nozzle assembly for post-test analysis. This "modified Type C" nozzle had more surface roughening in the throat area than the prior nozzle and might, therefore, be considered not as desirable on an overall basis.

To demonstrate the controlling influence of the reinforcing wires on improved insert performance, an additional nozzle was made with the same matrix material as the Type C composite but with no reinforcing wires. Compared with a 700-second test exposure with no erosion for the reinforced nozzle, the unreinforced nozzle experienced a 25% throat area increase in 7 seconds of test firing. This illustrates the extent to which wire reinforcement can improve the properties of a ceramic in a severe thermal shock environment such as a rocket nozzle. Based on the successful performance of these reinforced oxide throat inserts, recommendations are made concerning how this promising material might be used in specific advanced rocket nozzle applications.

INTRODUCTION

There is a continuing demand for improved materials for rocket nozzle inserts. For the highly-oxidizing hydrazine blend nitrogen tetroxide liquid propellant system, refractory oxides are promising materials for such inserts. These oxides have high-temperature capabilities, erosion-resistance, and the natural oxidation resistance necessary for this application. Their main shortcoming is their inherent brittleness which tends to cause catastrophic failure through thermal shock in a high heat flux application such as a rocket nozzle.

In a previous program (NASA Contract NAS 3-6280) that was aimed at testing a variety of material approaches for this type of application, TRW produced a fiber-reinforced oxide consisting of a partially-stabilized zirconia matrix reinforced with chopped 3.5-mil diameter W-3% Re wire. Small-scale (1.2 inch throat diameter) nozzle inserts of this composite containing 5-7 volume percent of the metal fiber were fabricated and tested; they showed a degree of durability superior to any other material tested prior to that time. The successful performance of these inserts resulted in further interest both in understanding the factors controlling the properties of the material and in determining the properties of this composite material in rocket engine tests of larger-scale inserts.

The present program, therefore, was aimed at optimizing and characterizing a zirconia-matrix, metal-fiber-reinforced composite material and at defining the processing technique required for fabrication of nozzle inserts of the composite material.

The following five-faceted approach was pursued in this program:

Task 1 - Processing Technique Development - A study of oxide matrix materials, reinforcement materials, and the processing of these components into sound composite structures.

Task 2 - Thermal Shock Tests - The evaluation of the thermal shock characteristics of the matrix materials and reinforced composites to aid in obtaining the optimum material and process variables.

Task 3 - Thermal and Mechanical Property Tests - Evaluation of the most promising composites for the mechanical and thermal properties of importance to rocket nozzle applications.

Task 4 - Oxidation Testing - An evaluation of the oxidation behavior of the composite material in propellant combustion products and in air.

Task 5 - Insert Design and Fabrication - Fabrication and test firing of 3" throat diameter inserts made from the most promising composite materials.

The following sections of this report describe the activity carried out in each of these areas.

TASK 1 - PROCESSING TECHNIQUE DEVELOPMENT

This part of the program was aimed at determining the best oxide matrix material, the best combination of reinforcement variables, and the best processing techniques for consolidating these constituents into optimum composite structures. This task was carried out integrally with the Task 2 thermal shock tests which provided the most decisive input for choosing the composite materials for further study in the program.

A. Matrix Materials

The throat inserts developed in this program are for a liquid rocket engine burning the propellants N_2O_4 and 50% UDMH-50% N_2H_4 . The surface of a throat insert made of an insulative material would be expected to reach 4600°F or higher during the firing of the rocket engine. This temperature requirement limits the choice of oxides to those of thorium, hafnium, and zirconium. On the basis of cost, availability, toxicity, and available technology, ZrO_2 was chosen as the most logical candidate for a fiber-reinforced composite matrix.

1. General Properties of Zirconia

The properties of consolidated ZrO_2 can be varied considerably depending on the end use of the product. This program included the design and characterization of a ZrO_2 product aimed specifically at the metal fiber-oxide matrix composite application. Both the chemical composition (amount and type of stabilizer) and the particle size of the starting powder are important parameters in controlling the properties of the consolidated matrix material of the composite nozzle insert.

Stabilizers - Pure (unstabilized) zirconia (ZrO_2) exists at room temperature in a monoclinic crystal structure. When heated above 2000°F, the crystal structure starts to change to a tetragonal structure. This crystal structure change is accompanied by a large decrease in volume as illustrated in Figure 1. This behavior limits the usefulness of pure zirconia in high heat flux applications since large stresses and resultant fracture occur in the ceramic body when one portion is trying to expand while another portion is trying to contract. To circumvent this difficulty, it is common to "alloy" a material like calcia (CaO) with the zirconia. This results in changing the material to a cubic crystal structure which is stable both at ambient and elevated temperature. The zirconia is thereby "stabilized".

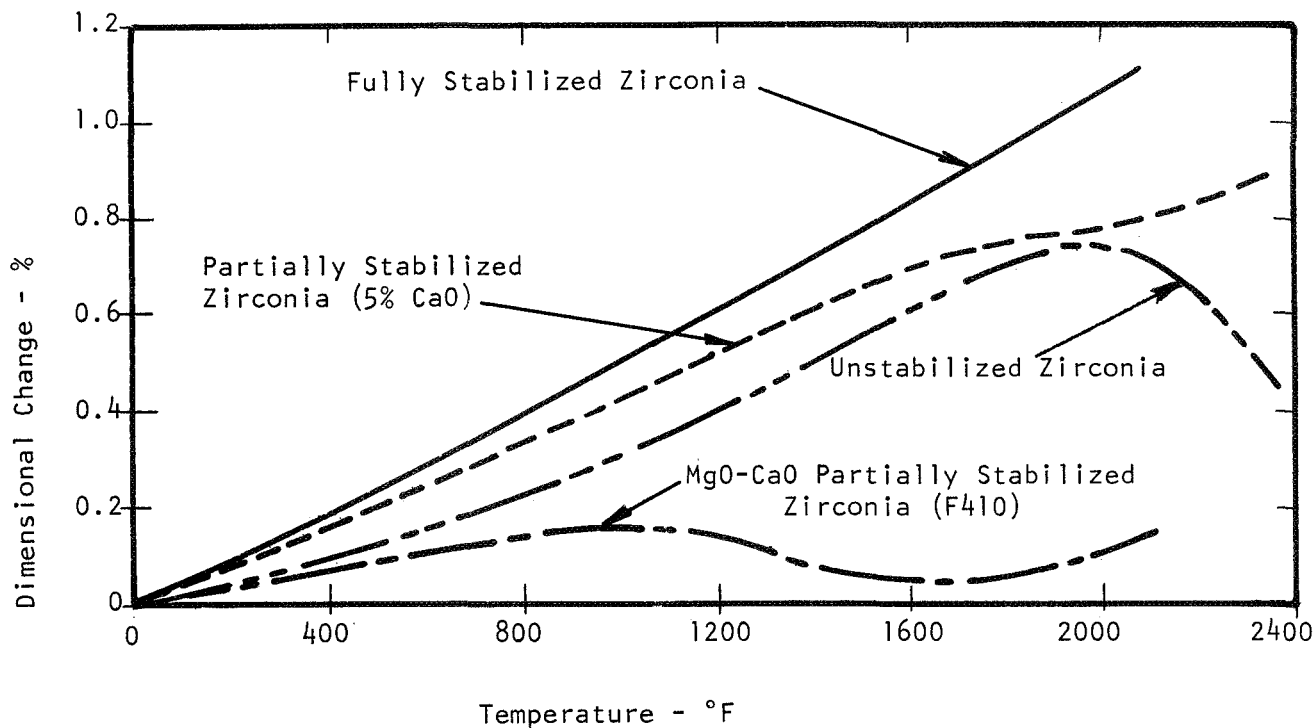


Figure 1. Thermal Expansion Properties of Selected Zirconia Compositions

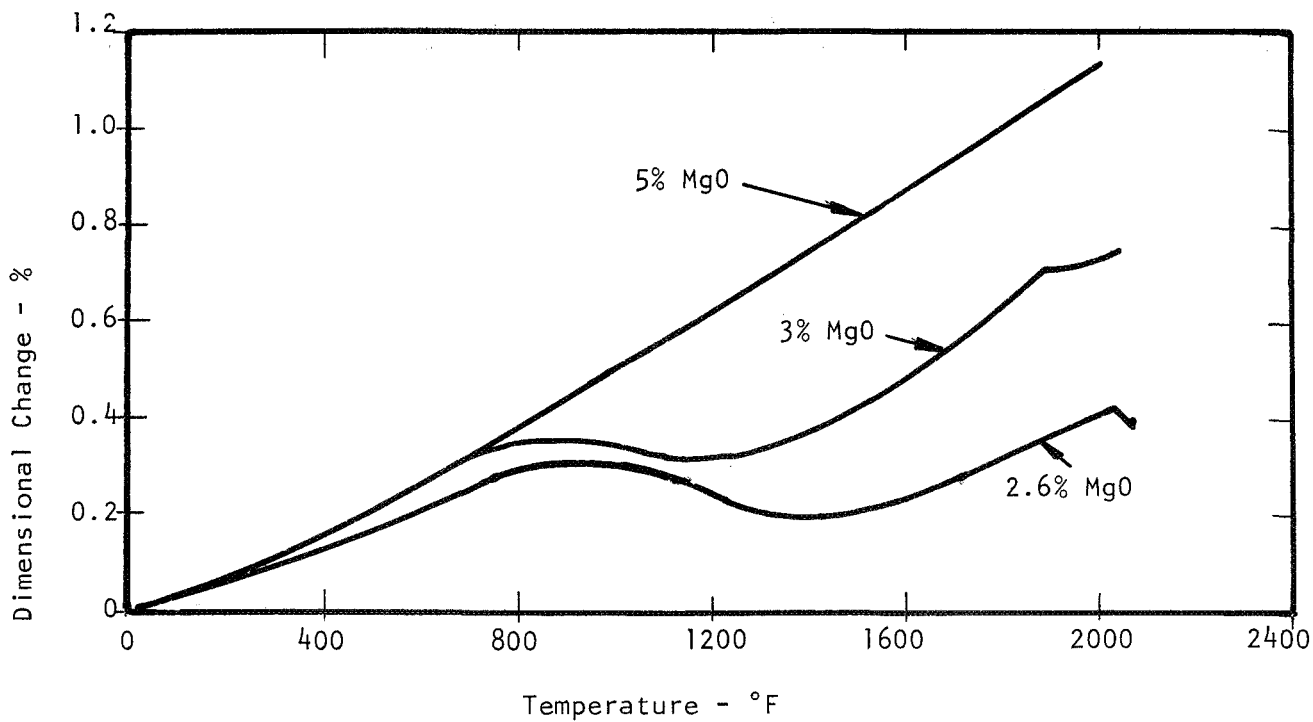


Figure 2. Thermal Expansion Heating Curves of Magnesia-Stabilized Zirconia

Fully-stabilized zirconia also has its drawbacks. Although it avoids the devastating crystal change, it does have a larger thermal expansivity than the unstabilized material (see Figure 1). If the material is only partially stabilized (by the addition of only 5% CaO, for example) a compromise in the low-temperature expansion behavior is achieved, and the partial transformation to the tetragonal form actually can improve the thermal properties at elevated temperature by flattening out the thermal expansion curve. Much of the technology of zirconia has been concerned with trying to improve the thermal stress properties of the material by controlling the type and amount of stabilizer additives.

One of the most promising stabilizers has been magnesia (MgO). A partially-stabilized MgO-ZrO₂ system not only undergoes the partial phase change in the 2000°F range, but it also undergoes a lattice relaxation phenomenon in the 1000°F range that results in a further flattening of the thermal expansion curve (Figure 2). Zircoa's F410 zirconia that was used in the previous reinforced-zirconia inserts fired at NASA-Lewis (Contract NAS 3-6280) is an MgO+CaO partially-stabilized zirconia (containing about 3% MgO and 0.5% CaO) chosen for its thermal expansion properties (Figure 1). Modifications of this material and of zirconia-base material with other stabilizers were included in the present program to find a matrix material with improved thermal properties for this application.

Powder particle size and texture - The particle size distribution of the starting powder coupled with the processing parameters will control the porosity characteristics of the final structure. Porosity in a ceramic structure tends to decrease the strength and modulus so as to reduce the elastic energy stored at fracture. A fracture will, therefore, have less energy with which to propagate through the structure. It is good ceramic practice to utilize coarse-grained, porous ceramics for thermal shock application.

In the rocket nozzle application being considered here, however, high density is desired for increased strength and erosion resistance, and for protection of the reinforcing wires from oxidation. Accordingly, relatively fine-particle zirconia powders (less than 10-micron diameter) were emphasized in this program.

Using these guidelines that a fine-particle, partially-stabilized zirconia was desired, this program included the following scope of activity in finding the optimum matrix material:

1. A survey and appropriate testing of commercially-available "off-the-shelf" zirconia powders.
2. The special formulation of about 20 compositions of zirconia by Zirconium Corporation of America (Zircoa).
3. The preparation by TRW of about a dozen specialized zirconia compositions.

2. Commercially-Available Zirconia

A survey indicated that compositions other than unstabilized or calcia-stabilized zirconia are generally not available as off-the-shelf items. This is not due to technical problems but reflects a lack of demand for commercial quantities of zirconia stabilized by oxides other than calcia. Most of the vendors contacted during the survey were not able to meet the fine particle size of zirconia powders considered necessary for high sintered densitites and good fiber-matrix bonding.

The zirconia compositions that were ordered as off-the-shelf items for evaluation during Task 1 are tabulated in Table 1. The as-received materials were examined by x-ray diffraction to determine the effects of the amount and type of stabilizer. The resultant data are included in Table 1. The percentage of cubic phase present in the composition was determined by measuring the intensity ratio of the III cubic/III monoclinic x-ray diffraction lines and comparing this with a standard plot obtained for mechanically blended mixtures of fully stabilized cubic and high-purity monoclinic zirconia powders. These powders were also characterized by particle size measurements with the Fisher Sub Sieve Sizer and with a Coulter Counter, and they were measured for surface area by the BET nitrogen absorbtion technique using a Perkin Elmer Sorptometer.

Samples were consolidated from these powders by isopressing at 30,000 psi and vacuum sintering for 4 hours at 4000°F to approximate the conditions anticipated for nozzle fabrication. They were then examined visually for general structural integrity.

The results of these tests are shown in Table 2. Sintered densities of the unreinforced compacts generally were dependent on the partical size of the powder. The comparatively low densities of the B₂O₃-stabilized and the Ti-stabilized compositions are due to the poor sintering characteristics of monoclinic zirconia. With the exception of the B₂O₃-stabilized material, all compositions were free from sintering cracks.

The sound compacts were screened by a thermal shock quench test. The thermal shock test used (more completely described in the Task 2 portion of this report) measures the maximum temperature from which a disc-shaped specimen (insulated on its flat face) can be quenched into salt brine without fracture of the specimen. These thermal shock results, presented later under the Task 2 part of this report, indicated that only F410 and the 6% Ti compositions were promising compared to other matrix materials.

Based on these results, these two compositions were tested for thermal expansion. The data are incorporated later in Table 6 where they are compared to other materials. In summary, as will be shown later in the discussion of thermal shock properties, only these two (F410 and 6% Ti) off-the-shelf compositions showed sufficient promise for further evaluation in reinforced composites.

TABLE 1

COMMERCIALY AVAILABLE ZIRCONIA COMPOSITIONS INCLUDED IN TASK 1

Composition	Vendor	w/o Cubic Phase*
4% MgO	Harbison-Walker	68
3% MgO	Zirconium Corporation of America	60
F410	"	56
6% MgO	"	100
3% CaO	Zirconium Corporation of America	52
5% CaO	Zirconium Corporation of America	95
8% Y_2O_3	Zirconium Corporation of America	92
12% Y_2O_3	Zirconium Corporation of America	100
10% Y_2O_3	H. T. M. Company (Zytritte)	100
6% Ti Metal	Consolidated Astronautics	0
3% B_2O_3	Consolidated Astronautics	0
Hi Purity Unstabilized	Zirconium Corporation of America	0

* Determined at TRW by x-ray diffraction techniques.

TABLE 2

PROPERTIES OF COMMERCIALY AVAILABLE ZIRCONIA COMPOSITIONS

Composition	ISOPRESSED AND VACUUM SINTERED 4 HOURS - 4000°F				
	Fisher Average Particle Dia., μ	BET Surface Area, M^2/g	Sintered Density, g/cc	% Theo Density	Comments
4% MgO Stabilized	2.7	1.02	5.29	92	Sound
6% MgO	6.6	1.42	5.20	87	Sound
3% MgO	2.5	1.405	5.61	93	Sound
5% CaO	3.1	1.14	5.32	94	Sound
3% CaO	3.0	0.856	5.44	92	Sound
8% Y_2O_3	9.0	2.53	4.98	84	Sound
12% Y_2O_3	4.8	0.432	5.25	86	Sound
6% Ti	0.7	0.321	5.18	86	Sound
3% B_2O_3	1.0	1.108	4.76	86	Cracked in Sintering
10% Y_2O_3 (Zyttrite)	Not Applicable*	4.28	-	-	Sound
Monoclinic ZrO_2	1.6	-	-	-	Uninterable
F410	1.1	2.99	5.30	92	Sound

* Measured by x-ray as 25 angstroms using Laue integral line breadth technique.

3. Special Zirconia Formulations by Zircoa

The Zirconium Corporation of America (Zircoa) of Solon, Ohio was subcontracted on this program to supply a series of 20 specialized zirconia compositions for this specific rocket nozzle application. The purpose of this subcontract was to allow Zircoa's specialized background and capabilities to be brought to play in this program. These special formulations include a series of zirconia compositions partially stabilized with MgO to take advantage of the low thermal expansion of this system. Three levels of MgO each in three particle size ranges comprised nine of these compositions. Three size ranges of a CaO-stabilized zirconia, and eight other various stabilizer systems accounted for the total of twenty lots of powder. The nine MgO-stabilized powders and the CaO-stabilized powders were prestabilized; i.e. the stabilizer was alloyed with the zirconia and the resultant material was subsequently crushed to the various particle size ranges. In contrast, the other compositions were supplied as monoclinic zirconia powder mechanically blended with powders of the various stabilizers.

These powders were tested for degree of stabilization and particle size as described above for the off-the-shelf compositions. Similarly, samples were isopressed and vacuum sintered to assess their general response to the sintering treatment and to obtain samples for thermal shock quench tests.

Data derived from the as-received and the sintered MgO and CaO-stabilized materials are tabulated in Table 3. The coarse and medium texture powders sintered to densities of 90 to 94% of theoretical while the fine textured materials reached densities of 96 to 98%. The data indicate that a high sintered density requires a material with a Fisher number of 1.6 microns or less and a particle size range of 80% less than 3.5 microns.

Particle size data for the other eight of the Zircoa series of compositions are shown in Table 4; the corresponding sinterability data are shown in Table 5. All of these materials were characterized by an extremely fine particle size and sintered to a high density. As noted in Table 5, most of this series of materials could not be sintered successfully. Two of the Y_2O_3 stabilized compositions, however, were sound and achieved essentially full theoretical density.

Bend strength and thermal expansivity data are shown in Table 6. Included in Table 6 are data derived from TRW-prepared zirconia compositions which will be discussed in the following section. Bend strength data, averaged from 10 specimens, show a wide range of values possibly caused by internal flaws present in certain of these compositions.

Specimens for thermal shock quench testing were machined from the sound specimens. All of the Zircoa-prepared compositions were tested with the exception of the 25% mixed rare earths and the CaO-modified materials which could not be sintered successfully.

TABLE 3

ZIRCONIA MATRIX COMPOSITIONS PREPARED BY ZIRCOA - MgO and CaO STABILIZERS

Major Stabilizer	Texture	X-Ray Diffraction Analysis % Cubic	Fisher Average Particle Diameter μ	Size Analysis		Sintered Density g/cc	% Theo	Comments on Sinterability
				Median* Particle Diameter, μ	80%-20%* Size Range, μ			
2.65% MgO	Coarse	69	2.7	21.5	40.0 - 14.0	5.5	93	Sound
2.65% MgO	Medium	72	2.5	11.0	30.0 - 6.0	5.5	94	Sound
2.65% MgO	Fine	62	1.6	2.2	3.5 - 1.6	5.7	98	Sound
2.85% MgO	Coarse	78	2.1	15.0	45.0 - 5.0	5.3	90	Sound
2.85% MgO	Medium	76	2.2	18.0	35.0 - 8.0	5.4	91	Sound
2.85% MgO	Fine	71	1.1	2.2	3.2 - 1.3	5.7	97	Sound
3.05% MgO	Coarse	83	2.2	17.0	43.0 - 7.0	5.4	92	Sound
3.05% MgO	Medium	83	2.0	12.0	30.0 - 5.0	5.5	93	Sound
3.05% MgO	Fine	77	1.2	1.9	2.8 - 1.1	5.6	96	Sound
4% CaO	Coarse	86	2.7	7.0	14.0 - 4.5	5.5	94	Sound
4% CaO	Medium	85	3.1	6.5	11.5 - 4.5	5.5	94	Sound
4% CaO	Fine	87	1.6	3.0	4.2 - 1.8	5.7	98	Sound

* Determined by Coulter Counter Analysis. The 80%-20% size range means that 20% (by weight) of the particles are larger than the upper end of the range indicated and 20% are smaller than the low end of the range.

TABLE 4

ZIRCONIA MATRIX COMPOSITIONS PREPARED BY ZIRCOA - VARIOUS STABILIZERS

AS-RECEIVED POWDER DATA					
Nominal Composition	X-Ray Diffraction Analysis of Powder	Fisher's Average Particle Diameter, μ	BET Surface Area M^2/g	Size Analysis	
				Median* Particle Diameter, μ	80%-20%* Size Range, μ
6% Y_2O_3	Monoclinic + Cubic Rare Earth Oxide (Ho_2O_3 + Y_2O_3)	1.57	1.18	1.6	2.5 - 1.0
8% Y_2O_3	Monoclinic + Y_2O_3 and Trace Cubic	1.57	1.43	1.5	2.3 - 1.0
15% Rare Earths	Monoclinic + compounds of Sm_2O_3 Type Structure and Trace Cubic	1.25	3.13	1.6	2.5 - 1.0
25% Rare Earths	Monoclinic + Mixture of Cubic Rare Earths of Mn_2O_3 Type Structure and Complex Structure Not Identified	0.8	3.40	1.5	2.5 - 1.0
10% CeO_2	Monoclinic ZrO_2 + CeO_2	1.6	1.21	1.5	2.3 - 1.0
20% CeO_2	Monoclinic ZrO_2 + CeO_2 Approximately 80/20	1.3	1.21	1.6	2.4 - 1.0
CaO Modified	55% Cubic	1.5	1.53	1.8	3.3 - 1.0
Y_2O_3 Modified	Mostly Monoclinic ZrO_2 + Cubic (Ho_2O_3 + Y_2O_3) Structure	1.9	0.80	1.6	2.5 - 1.0

* Determined by Coulter Counter

TABLE 5

ZIRCONIA MATRIX COMPOSITIONS PREPARED BY ZIRCOA - VARIOUS STABILIZERS

Nominal Composition	SINTERED PROPERTY DATA			Comments on Sinterability
	Sintered Density g/cc	% Theo	% Cubic As Sintered	
6% Y_2O_3	5.8	98	95	Circumferential Crack at Midpoint
8% Y_2O_3	5.8	98	100	Sound
15% Rare Earths	5.1	90	87	Small Surface Cracks
25% Rare Earths	5.4	89	--	Large Axial Cracks
10% CeO_2	5.9	90	28	Small Circumferential Cracks
20% CeO_2	5.6	87	57	Sound
CaO Modified	5.3	90	--	Large Crack
Y_2O_3 Modified	5.6	96	100	Sound

TABLE 6

PROPERTIES OF UNREINFORCED ZIRCONIA MATRIX MATERIALS
AFTER VACUUM SINTERING FOR 4 HRS. @ 4000°F

Matrix Material	Texture	Avg. Grain Diameter Microns	Bend Strength as Sintered ksi	Therm. Expansion in/in/°C x 10 ⁶ 100° - 1300°C
2.65 MgO	Coarse	80	1.392	8.4
2.65 MgO	Medium	105	45.708	8.9
2.65 MgO	Fine	100	6.851	8.9
2.85 MgO	Coarse	80	1.066	7.3
2.85 MgO	Medium	75	1.483	7.2
2.85 MgO	Fine	155	35.177	9.7
3.05 MgO	Coarse	130	1.236	8.5
3.05 MgO	Medium	90	-	6.9
3.05 MgO	Fine	130	44.679	10.1
3.5 CaO	Coarse	95	40.566	10.7
3.5 CaO	Medium	130	46.591	10.2
3.5 CaO	Fine	115	29.179	10.3
3% Y ₂ O ₃		130		8.0
5% Y ₂ O ₃		37		2.5
6% Y ₂ O ₃		105		9.8
8% Y ₂ O ₃		95		10.2
Y ₂ O ₃ Modified		90		-
5% CeO ₂		190		8.6
10% CeO ₂		120		0.9
10% CeO ₂		260		2.0
20% CeO ₂		165		7.8
15% Mixed Rare Earths		105		10.4
6% Ti		150		8.6
5% Ti		120		7.8
5% Zr				.
5% Hf				.

The details of the thermal shock testing are presented under Task 2. In summary, the 2.65% MgO fine-textured and 2.85% MgO medium-textured materials showed the most promise for further evaluation, and these two compositions were included in the composite reinforcement portion of the program.

4. Zirconia Compositions Prepared at TRW

The survey of available matrix materials had indicated that a limited choice of compositions and powder particle size ranges was available commercially. As a backup to Zircoa's efforts, an additional series of compositions incorporating various stabilizer systems was prepared by TRW for evaluation. These materials are summarized in Table 7. The compounds were processed by isostatic pressing and vacuum sintering mechanical blends of commercially available cubic and monoclinic zirconia materials in a single step process. This brief exploratory study was undertaken to permit a greater degree of flexibility in the choice of stabilizer materials and material sources.

Preliminary judgement based on the appearance, density and freedom from gross cracking of the sintered specimen indicated that the use of a single step process is feasible. The presence of the stabilized zirconia fraction apparently suppresses the damaging volume change which occurs during the phase transformation and permits the sintering of a sound crack-free compact. Compositions fabricated from monoclinic zirconia containing low levels of stabilizers (5% CeO₂, 3% MgO, and 3% Y₂O₃) contained internal cracks and large voids or fissures. Higher levels of stabilizer content were not as susceptible to this type of cracking. With the exception of the 3% MgO and 6% Y₂O₃ compositions, all of this series of materials were evaluated by thermal shock quench testing. On the basis of the quench test, the 3 and 5% Y₂O₃ and 5 and 10% CeO₂ compositions were included in the composite reinforcement program, and the balance of this series of compositions were dropped from the program. (The thermal expansion results of these Y₂O₃ and CeO₂ compounds were included in Table 6).

The matrix materials prepared by TRW together with those previously discussed were examined by x-ray diffraction to determine the effects of the amount and type of stabilizer. The percentage of cubic phase present in the composition was determined by, as described earlier, the intensity ratio of the 111 cubic/111 monoclinic x-ray diffraction lines. The amount of cubic phase present is plotted as a function of stabilizer content for MgO, CaO, CeO₂, Y₂O₃ stabilizer systems and presented in Figure 3. Zircoa's F410 composition previously used as the matrix material for tungsten fiber reinforced composites is also included in Figure 3. The data indicate that the degree of stabilization is sensitive to small amounts of MgO, CaO and Y₂O₃ and relatively insensitive to Ti metal, CeO₂ and the mixed rare earth additions.

TABLE 7

ZIRCONIA MATRIX COMPOSITIONS PREPARED BY TRW BY THE
SINGLE STEP PROCESS OF MIXING, PRESSING, AND SINTERING OF CONSTITUENT POWDERS

Stabilizer System	Blend Materials (by weight)	Sintered Density		Comments of Sinterability
		g/cc	% Theo.	
10% CeO ₂	90% Monoclinic ZrO ₂ 10% CeO ₂	5.08	90	Sound
5% CeO ₂	95% Monoclinic ZrO ₂ 5% CeO ₂	5.35	94	Internal Fissures
6% Y ₂ O ₃	94% Monoclinic ZrO ₂ 6% Y ₂ O ₃	5.30	93	Cracked
5% Y ₂ O ₃	95% Monoclinic ZrO ₂ 5% Y ₂ O ₃	5.33	93	Sound
3% Y ₂ O ₃	97% Monoclinic ZrO ₂ 3% Y ₂ O ₃	5.46	96	Porous Core and Fissures
3% MgO	97% Monoclinic ZrO ₂ 3% MgO	5.20	91	Cracked
3% MgO 0.5% CaO	50% 4%-MgO-Stabilized ZrO ₂ 10% 5%-CaO-Stabilized ZrO ₂ 1% MgO	5.29	93	Sound
3% MgO 1% CaO	39% Monoclinic ZrO ₂ 50% 4%-MgO-Stabilized ZrO ₂ 20% 5%-CaO-Stabilized ZrO ₂ 1% MgO	5.26	92	Sound
3% MgO 2% CaO	29% Monoclinic ZrO ₂ 50% 4%-MgO-Stabilized ZrO ₂ 40% 5%-CaO-Stabilized ZrO ₂ 1% MgO	5.12	90	Sound
	9% Monoclinic ZrO ₂			

TABLE 7 (Cont'd)

Stabilizer System	Blend Materials (by weight)	Sintered Density, g/cc	Sintered Density, % Theo	Comments of Sinterability
4% MgO 0.5% CaO	50% 4%-MgO-Stabilized ZrO ₂ 10% 5%-CaO-Stabilized ZrO ₂ 2% MgO 38% Monoclinic ZrO ₂	5.19	91	Sound
4% MgO 1% CaO	50% 4%-MgO-Stabilized ZrO ₂ 20% 5%-CaO-Stabilized ZrO ₂ 2% MgO 28% Monoclinic ZrO ₂	5.13	90	Sound
4% MgO 2% CaO	50% 4%-MgO-Stabilized ZrO ₂ 40% 5%-CaO-Stabilized ZrO ₂ 2% MgO 8% Monoclinic ZrO ₂	5.11	90	Sound

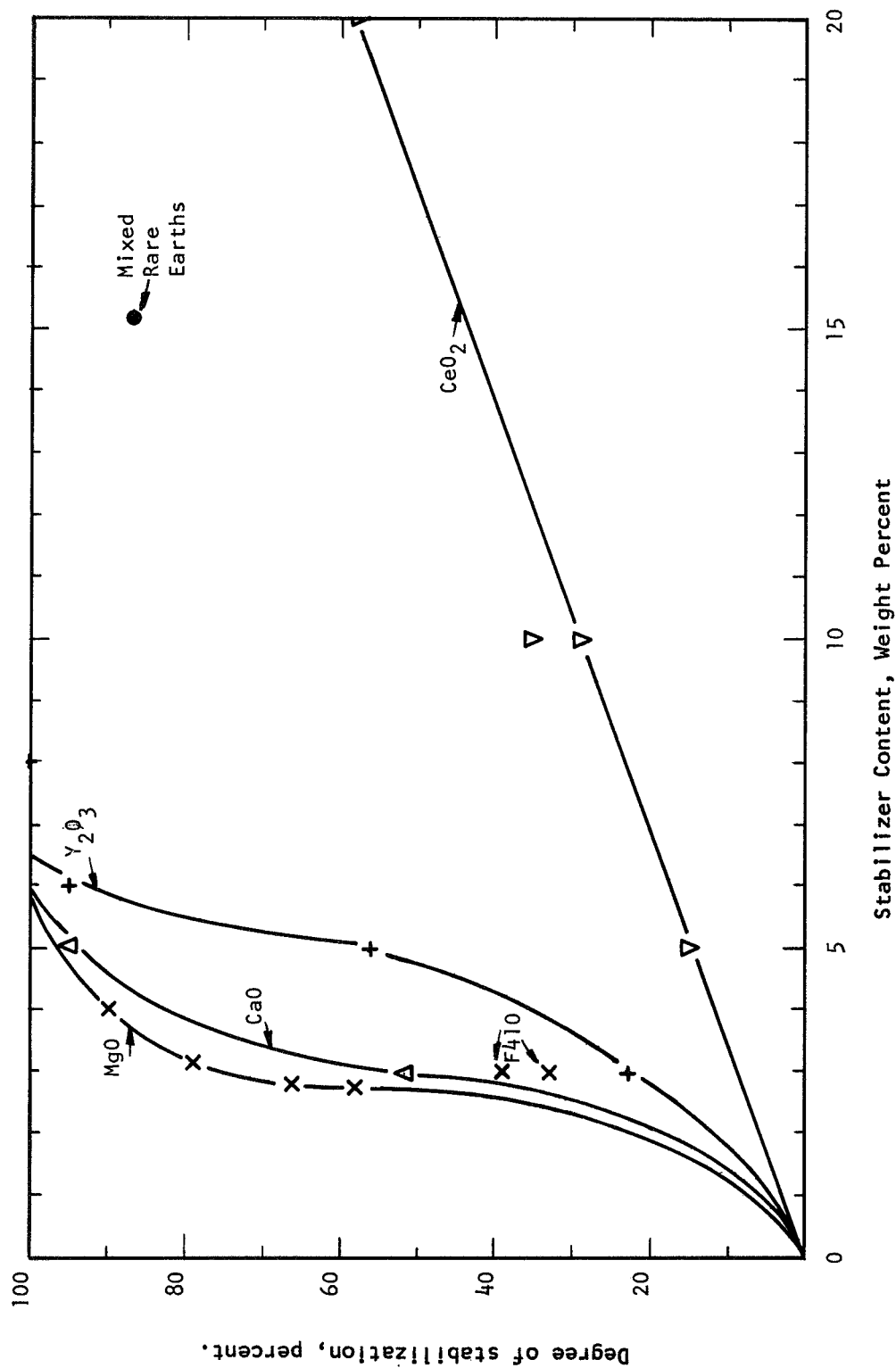


Figure 3. The stabilizing effects of various oxides on monoclinic zirconia after a 4 hour - 4000°F vacuum sintering treatment.

5. Matrix Material Selection

From the three categories of off-the-shelf, Zircoa-prepared, and TRW-prepared materials, a total of 42 zirconia compositions were tested in this part of the program. Based on the data discussed above together with the thermal shock results detailed in the Task 2 part of this report, the following materials were found to be the most promising for further study in the program.

Prestabilized Materials: 3% MgO Commercial from Zircoa
F410 (MgO + CaO) Commercial from Zircoa
Zircoa's 2.65% MgO Fine Texture
Zircoa's 2.85% MgO Medium Texture

Single Step Compounds: 3% Y_2O_3 Prepared by TRW
5% Y_2O_3 Prepared by TRW
5% CeO_2 Prepared by TRW
10% CeO_2 Prepared by TRW

Monoclinic: 6% Ti Commercial from Consolidated
Astronautics

These matrix materials were the ones of prime interest for evaluation in the form of fiber reinforced composites in the subsequent parts of the program.

B. Reinforcement Materials

A ductile metal reinforcing material was composited with the brittle zirconia matrix in this program to endow the composite with resistance to thermal shock. The scope of this program was limited to the use of chopped wires of the reinforcement randomly distributed throughout the zirconia matrix. These ductile metal fibers can improve the brittle fracture resistance of the zirconia by arresting cracks and forcing them to reinitiate or change direction. These processes absorb energy and thereby improve the fracture toughness of the composite. As microcracking of the matrix takes place during thermal cycling, the stress can be transferred from the brittle matrix to the more ductile fiber. This process provides a strain mechanism in the composite which allows it to behave as a more ductile material.

The properties required in such a reinforcing material are stringent. A candidate material must have a high melting point, ductility, high strength, and high elastic modulus coupled with sufficient oxidation resistance and compatibility with the matrix material to withstand both the fabrication conditions and the operating environment of the nozzle insert. The most likely candidates for this application include the alloys of tungsten, molybdenum, columbium, and rhenium. Tantalum, which also has a high melting point, cannot be considered because it is reactive with zirconia at the 4000°F temperature range anticipated for sintering of the composite structure. Except for rhenium, the other platinum metals cannot seriously be considered because of cost.

1. Materials Studied

An availability survey of reinforcing materials of these above-mentioned categories was carried out during Task 1. The materials that were subsequently procured for evaluation are listed in Table 8. These wires were purchased in continuous lengths of 3.5 mils diameter insofar as availability allowed. This diameter was chosen for the preliminary evaluation of these materials based on prior experience with this type of composite. Certain alloys were not available in diameters of less than 10 mils, so they were purchased and evaluated in the 10-mil diameter size.

The survey indicated that the most ready source of refractory metal wire of the size range of interest is the lamp industry. (Sylvania, G.E. etc.). It was evident that wires not produced by these sources are not available in quantity at reasonable cost. For instance, rhenium wire, a potentially attractive reinforcement material, was not available in the 3.5 mil diameter size. The smallest diameter available was 10 mils, and the cost of that was prohibitive for serious consideration for this program.

2. Evaluation Procedures

The materials listed in Table 8 were evaluated initially on the basis of their ability to resist degradation resulting from thermal treatments typical of composite fabrication processes. Accordingly, these wires were evaluated not only in the as-received condition but also after thermal treatments in vacuum of 30 minutes at 3000°F (a typical hot press cycle) and of 4 hours at 4000°F (a typical sintering cycle). After such treatments, the wires were evaluated by metallography and by tensile tests performed at room temperature and at elevated temperatures up to 4500 °F.

The tensile testing of these wires was conducted on an Instron tensile machine. Specimens for room-temperature testing were epoxy-bonded to sheet metal tabs containing a cross-pin hole grip. A 3-inch gage length was used with a cross head speed of 0.02 inches per minute. Yield strengths were plotted from the load-deflection curves using a 0.2% offset. Elongation measurements were also derived from the load-deflection curves.

For the elevated-temperature tests, mechanical grips were used. These tests were conducted in a transparent quartz tube with a mixture of 75% Ar - 25%He as a protective atmosphere. Specimens were heated by self resistance. The temperatures were measured with an optical pyrometer. Emissivity values of 0.375 at 2500°F and 0.367 at 4500°F were used in correcting temperature readings of the W wires. A value of 0.30 was used for Mo. A 3-inch gage length and a cross head speed of 0.02 inches per minute were used for all elevated temperature testing. Yield strength (0.2% offset) and elongation measurements were made from the load-deflection curves.

TABLE 8

FIBER REINFORCEMENT MATERIALS

OBTAINED AS CONTINUOUS LENGTHS FOR PRELIMINARY EVALUATION

W-doped (218 W)	3.5 mil	General Electric
W-25% Re	3.5 mil	Rember Co., Inc.
W-5% Re	3.5 mil	Hoskins Mfg. Co.
W-3% Re	3.5 mil	General Electric
W-1.5% Re	3.5 mil	Sylvania
W-1% ThO ₂	3.5 mil	General Electric
Mo-unalloyed	3.5 mil	Sylvania
Mo-TZM	3.5 mil	Sylvania
Mo-50% Re	3.5 mil	Rember Co., Inc.
Cb-unalloyed	3.0 mil	Armetco
Cb-30% Zr	5.0 mil	Armetco
Cb-15% Zr	10.0 mil	Armetco
Cb-10% Zr	5.0 mil	Armetco
Zr-unalloyed	10.0 mil	Armetco

3. Results of Evaluation

Tensile results - The columbium, zirconium, and their alloys were embrittled by the 30 minute - 3000°F treatment to such a degree that they could not be tensile tested. These wires were, therefore, dropped from further consideration in this program. The tungsten and molybdenum alloys generally retained sufficient strength and ductility to allow subsequent tensile testing. The results of such tests are listed in Table 9. This table includes the room temperature and elevated temperature properties of 3.5 mil wire in the as-received condition as well as after the vacuum treatments of 3000 and 4000°F. The small loads involved in measuring the tensile properties of a 3.5 mil diameter wire with a strength level of less than 15,000 psi made the accuracy of these measurements questionable. Consequently, all wires having an ultimate tensile strength under 15,000 psi are so listed with no further estimate of actual strength. The elevated temperature tests of Mo and Mo-alloy wires in the vacuum heat treated condition could not be performed because the wires were too fragile to permit mounting for the tests.

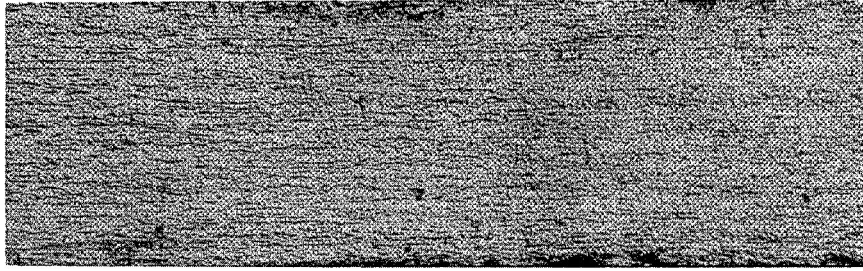
As the data in Table 9 indicate, the room temperature strength levels of the W alloy wires are reduced approximately 50% by the 3000°F - 30 minute vacuum treatment. The elevated temperature strengths in most cases, however, are virtually unaffected by this treatment. The 4000°F treatment reduced the strength of these wires even further, but, again, this effect is diluted at the higher testing temperatures. This evaluation shows that, among the several classes of materials considered for reinforcement, only the tungsten alloys retain sufficient strength and ductility after high-temperature exposure to be considered as effective reinforcements for a zirconia matrix-composite.

Recrystallization behavior - The W-5% Re and W-25% Re together with the molybdenum alloys were the ones that showed the greatest degradation in tensile properties after high-temperature exposure. This effect is attributed to recrystallization. The W-5% Re and W-25% Re alloys were produced as thermocouple wire and are, therefore, undoped. The lamp wire manufacturers, in contrast, customarily dope their tungsten alloys with small additions of K, Al, and Si to inhibit recrystallization and to promote the formation of elongated, interlocked grains when recrystallization does occur. In fact, the 218W (a doped tungsten from General Electric), W-1% ThO₂, W-15% Re, and W-3% Re alloys included in this program were manufactured as lamp wire. The microstructures of these various W-Re alloy wires after the 3000°F treatment are shown in Figure 4. The fibrous microstructure of the W-1.5%Re and the W-3% Re doped alloy wires is consistent with their superior properties after high-temperature exposure. The undoped W-5% Re and W-25% Re compositions accordingly show the equiaxed recrystallized microstructure indicative of brittle behavior in these alloys. A fibrous microstructure is also characteristic of the doped unalloyed W (218 W) and the W-1%ThO₂ wire after the 3000°F treatment. These microstructures are compared with the Mo alloys in Figure 5. The Mo, MoTZM, and Mo-50%Re alloy wires are completely recrystallized by the 3000°F exposure as is indicated by their inferior tensile properties.

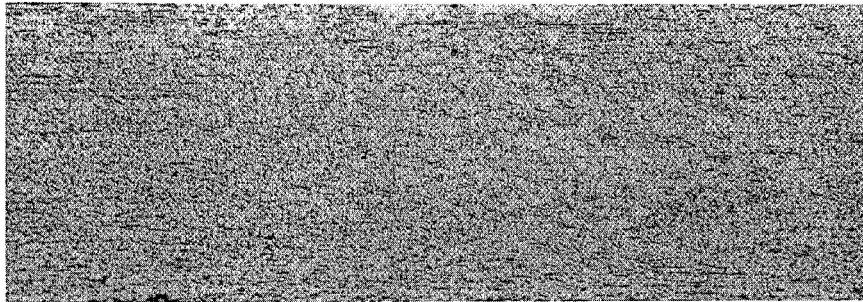
TABLE 9

TENSILE PROPERTIES OF VACUUM TREATED 3.5 MIL DIAMETER WIRE
TESTED AT VARIOUS TEMPERATURES

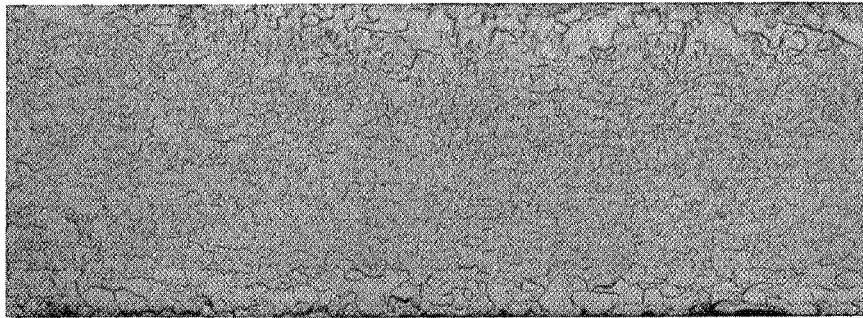
Material	Property	As-Received Wire			After Treatment of 30 Minutes @ 3000°F			After Treatment of 4 Hours @ 4000°F		
		R.T. 2500°F 3500°F 4500°F			R.T. 2500°F 3500°F 4500°F			R.T. 2500°F 3500°F 4500°F		
		UTS	Yield	Elongation %	UTS	Yield	Elongation %	UTS	Yield	Elongation %
218W	UTS	382	88		177	69	28.4	121	36.1	26.0
	Yield	359	88		177	69	27.9	121	33.8	26.0
	Elongation %	0.4	1.0		0.1	0	1.3	0	0.4	0.1
W-1.5% Re	UTS	327	121		190	77	34.2	148	41.3	19.5
	Yield	287	121		190	77	33.9		33.9	19.5
	Elongation %	0.4	0.7		0	0	4.4		0.4	0.2
W-3% Re	UTS	434	61		190	62	35.0	177	42.7	24.7
	Yield	400	61		190	62	33.8	177	37.9	24.7
	Elongation %	0.2	1.0		0.2	0	0.8	0	1.0	0.2
W-5% Re	UTS	255	103		134	41	20.2	107	37.9	33.3
	Yield	248	-		134	35	16.1	-	32.2	33.2
	Elongation %	0.9	-		0.1	1.0	2.0	-	0.6	0.6
W-25% Re	UTS	400	197		200	44	22.3	154	41.6	17.6
	Yield	400	177		200	44	21.6	-	41.6	17.6
	Elongation %	0	3.7		0	1.7	4.5	-	0	0
W-1% ThO ₂	UTS	300	79		237	64	18.3	133	33.1	17.8
	Yield	293	79		238	64	18.3	133	28.8	17.8
	Elongation %	0.4	1.6		0	0.1	1.3	0	0.6	0.1
Mo	UTS	105	25		37	34	-	30	-	-
	Yield	70	21		34	-	-	-	-	-
	Elongation %	17.0	2.0		0.7	-	-	-	-	-
Mo-TZM	UTS	185	98		112	25	-	-	-	-
	Yield	178	-		-	-	-	-	-	-
	Elongation %	0.7	-		-	-	-	-	-	-
Mo-50% Re	UTS	240	66		150	25	-	110	-	-
	Yield	240	63		150	25	-	110	-	-
	Elongation %	0.1	6.7		0	3.0	-	0	-	-



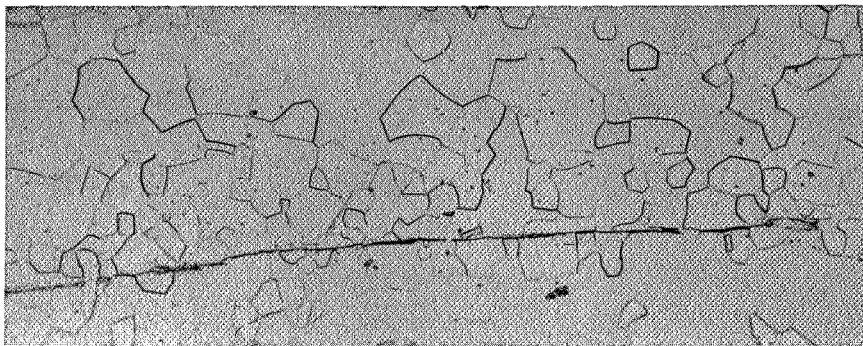
W-1.5%Re
(doped)



W-3%Re
(doped)

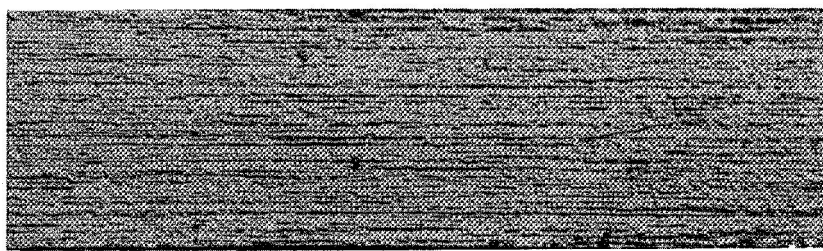


W-5%Re
(undoped)

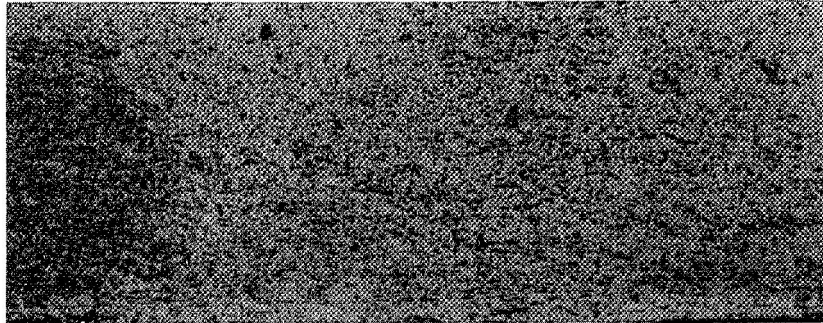


W-25%Re
(undoped)

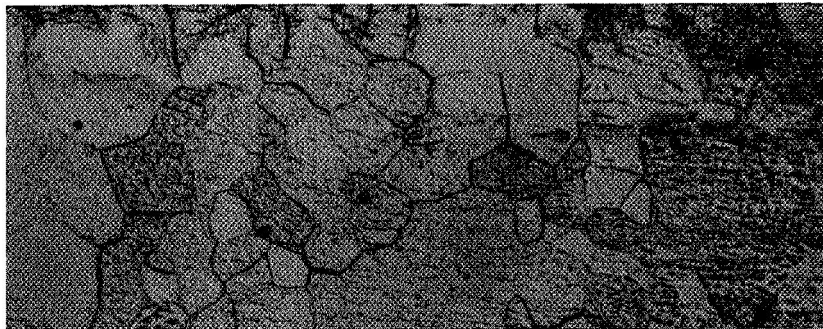
Figure 4. Microstructure of W-Re alloy wires after a 3000°F-30 minute vacuum heating cycle. 500X



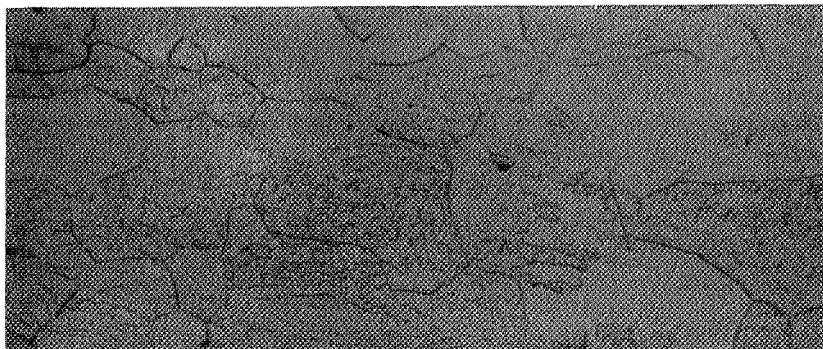
218W
(doped W)



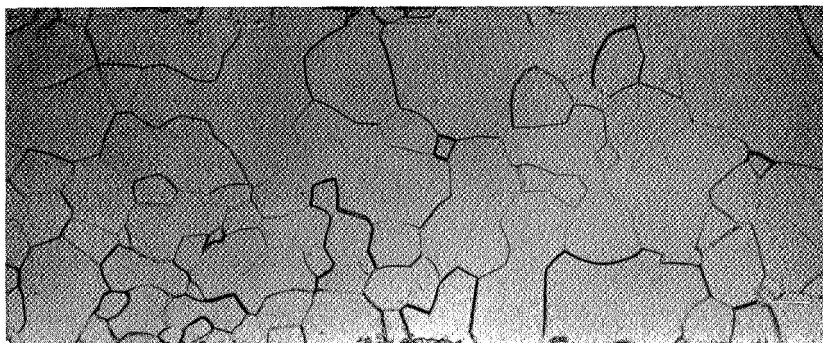
W-1%ThO₂
(doped)



Mo
(undoped)



MoTZM
(undoped)



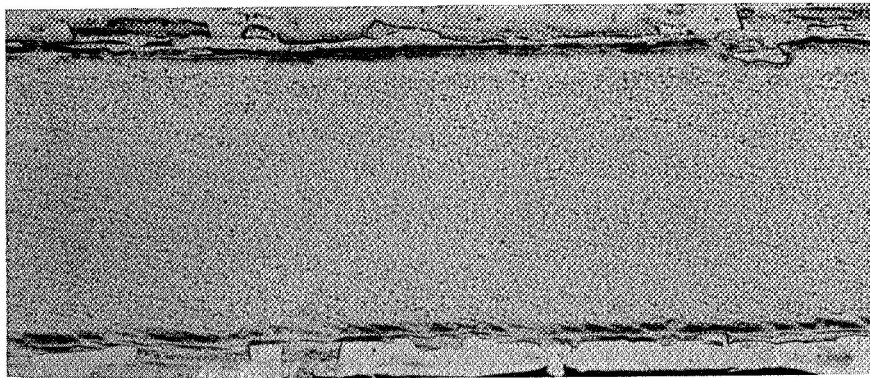
Mo-50%Re
(undoped)

Figure 5. Microstructure of W and Mo alloy wires after a 3000°F-30 minute vacuum heating cycle. 500X

All wires were completely recrystallized by the 4000°F-4 hour vacuum treatment, and all wires underwent brittle failure during subsequent room temperature tensile testing. Tensile data do not indicate superior hot strengths of any of the recrystallized W alloys. The doped alloys exhibit improved ductility at elevated temperatures. In this respect, the 1.5 and 3% Re alloys are somewhat superior. The microstructures of the W-Re alloys are presented in Figure 6. Figure 7 shows the microstructures of the doped unalloyed W, W-1%ThO₂, and Mo-50% Re alloys. These photomicrographs indicate effects of doping on the grain structure. The doped alloys are characterized by large interlocking grains while the undoped alloys show an equiaxed microstructure.

4. Selection of Best Reinforcement Material

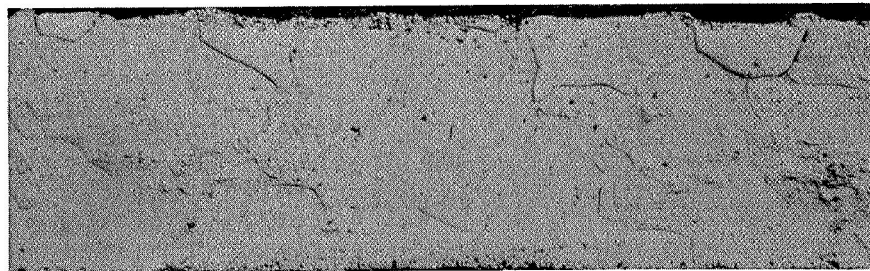
The tensile data presented in Table 9 indicate that several of the doped tungsten alloys retain significant properties after high-temperature exposure. In choosing the best one for use in subsequent parts of the program, the following criteria were established. First it was assumed that the 4000°F-4 hour sintering treatment was most likely to be used for composite processing, so that the properties after this treatment should be the primary consideration. Next, the function of these fibers in a rocket nozzle insert was considered. In a nozzle firing, the I.D. of the nozzle insert will be heated by the exhaust gases and attempt to expand. The relatively cool O.D. will therefore, be placed under a tensile hoop stress. It is this stress that will cause catastrophic failure in a nozzle made of a brittle material such as zirconia, so it is this stress that the reinforcing wires must accommodate. Since this hoop stress will likely be the greatest when the O.D. of the nozzle is coolest, it is the room temperature tensile strength of the reinforcing wires (after the 4000°F-4 hour treatment) which was used as the criterion for choosing the best reinforcing material. Using this criterion, the W-3% Re was chosen as the reinforcement for use in the remainder of the program (see Table 9 for the tensile data after the 4000°F treatment). This alloy also has relatively good elevated-temperature properties after this treatment, so it should serve as a good reinforcement in both the hot and cold parts of a nozzle insert during the firing cycle.



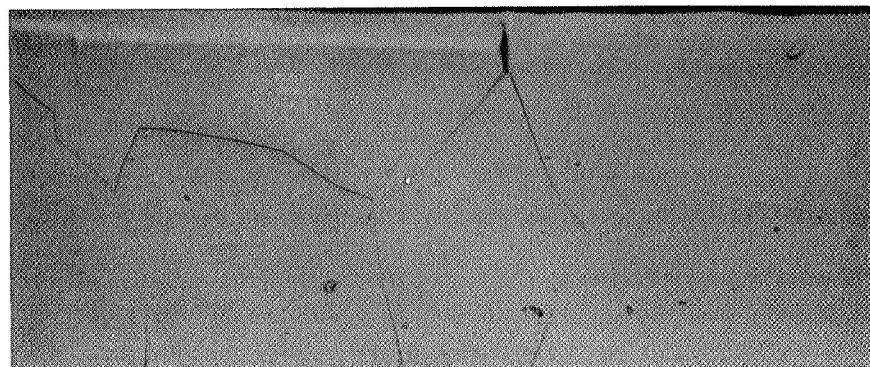
W-1.5%Re
(doped)



W-3%Re
(doped)

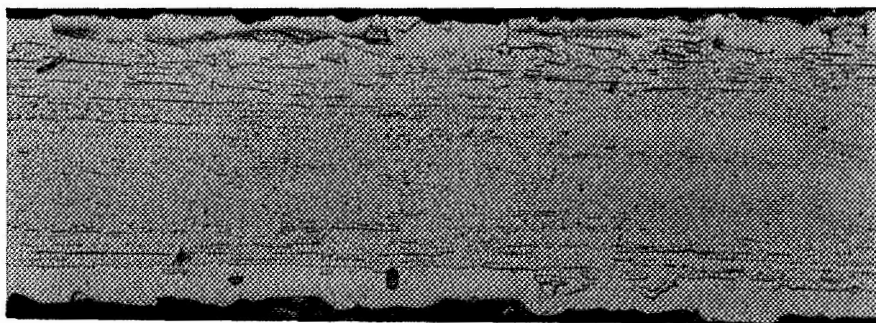


W-5%Re
(undoped)

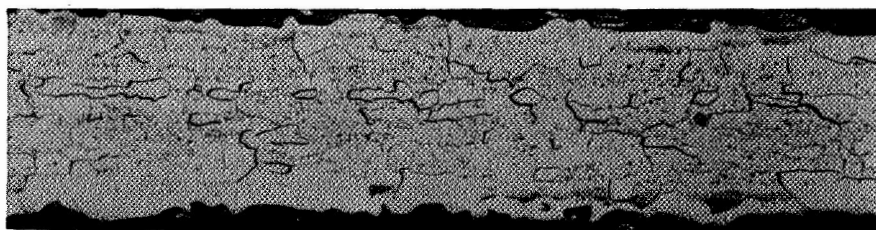


W-25%Re
(undoped)

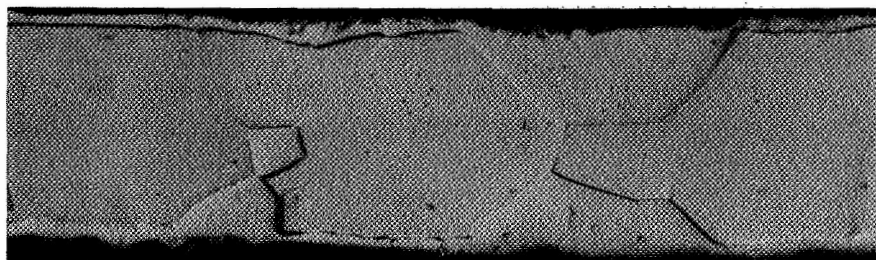
Figure 6. Microstructure of W-Re alloy wires after a 4000°F-4 hour vacuum heating cycle. 500X



218W
(doped W)



W-1%ThO₂
(doped)



Mo-50%Re
(undoped)

Figure 7. Microstructure of W and Mo alloy wires after a 4000°F - 4 hour vacuum heating cycle. 500X

C. Composite Fabrication

After having identified a number of promising zirconia matrix materials and the best available reinforcement material, the task remained to determine the best processing and material variables for producing optimum composites from these materials. Even with the limited scope of considering only chopped wires for reinforcement, variables such as the amount of reinforcement, the diameter and length of reinforcing wires, and the composite fabrication parameters had to be evaluated. In order to carry out this investigation efficiently, choices of parameters to be studied were based on past experience wherever possible. For example, in studying the effect of amount and diameter of reinforcing wires, one typical matrix material and one length/diameter ratio (aspect ratio) wire was used. Similarly, in studying consolidation procedures, we used only one isopressing and vacuum sintering treatment combination that was based on prior experience. As an alternate processing approach, hot pressing was investigated. The work performed in these two areas of reinforcement variables and hot pressing procedures is summarized below.

1. Reinforcement Variables

A series of composites using F410 zirconia as the matrix material and reinforced with W-3% Re wires were fabricated by isopressing and vacuum sintering. The composites contained 3, 5, 10, and 20% by volume of chopped wires of 2, 3.5, 5, and 10 mils diameter. The aspect ratio was maintained at about 60. These composites were fabricated by blending the chopped wires with the zirconia powder and then isopressing at 30,000 psi followed by a 4000°F - 4 hour vacuum sintering treatment.

The sintered densities of these composites are shown in Figure 8 as a function of wire volume. The trend toward lower densities with increasing volume of metal wires is probably caused by the formation of a metal-wire skeleton support which prevents free shrinkage of the matrix material during sintering. Composites containing 20% by volume (20 v/o) of metal wires could not be blended to form homogeneous composites. The composite of 20 v/o 5-mil wire could not even be sintered because of the poor compressibility during compaction. The 20 v/o 10-mil wire compact was sinterable only because the metal wires formed a skeleton that was self supporting. There was virtually no fiber-matrix integrity in this compact. Thus, it appears that a 20 v/o is not applicable to these composites fabricated by an isopress-and-sinter approach.

Discs for thermal shock quench tests were machined from each of these specimens. Photographs of the untested specimens are presented in Figures 9, 10, 11, and 12. It is apparent from the appearance of these specimens that with increasing wire diameter and/or increasing wire content the fiber-matrix bond is deteriorating. Metallographic examination and transverse rupture tests of the as-sintered material and of the thermal shock tested material were performed to define the effects of wire diameter and content on the properties of the composite. Petrographic techniques were also used to study the significant structural characteristics of these materials.

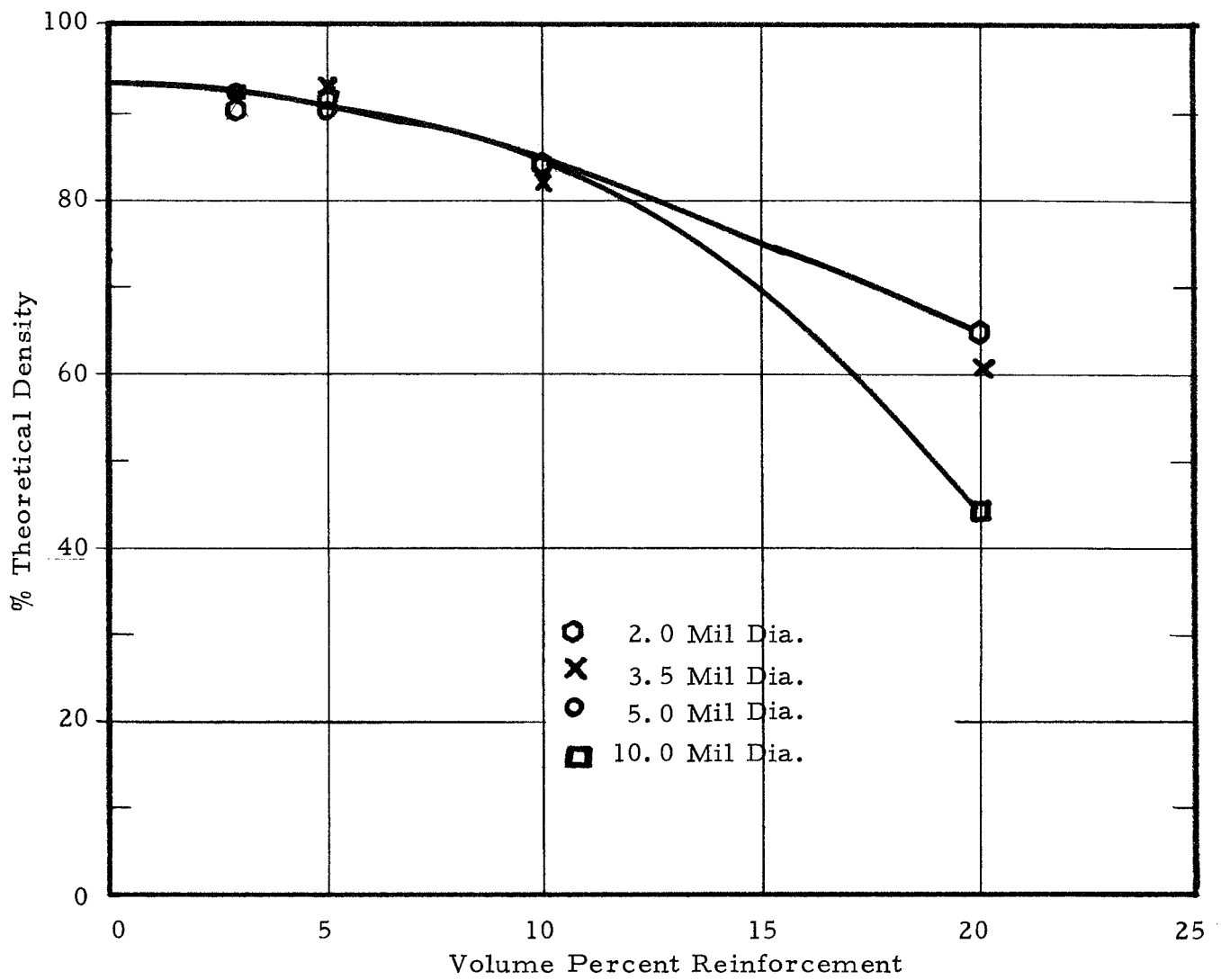
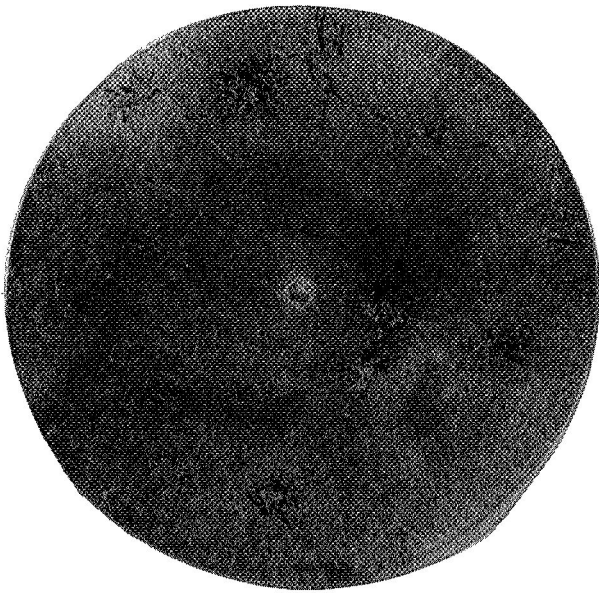
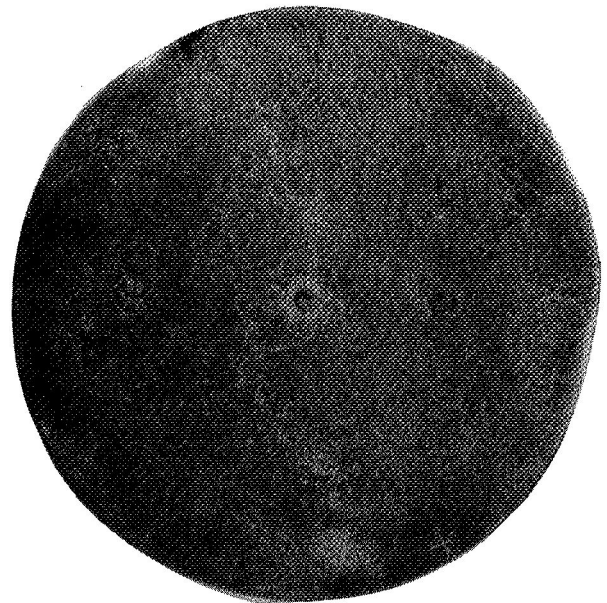


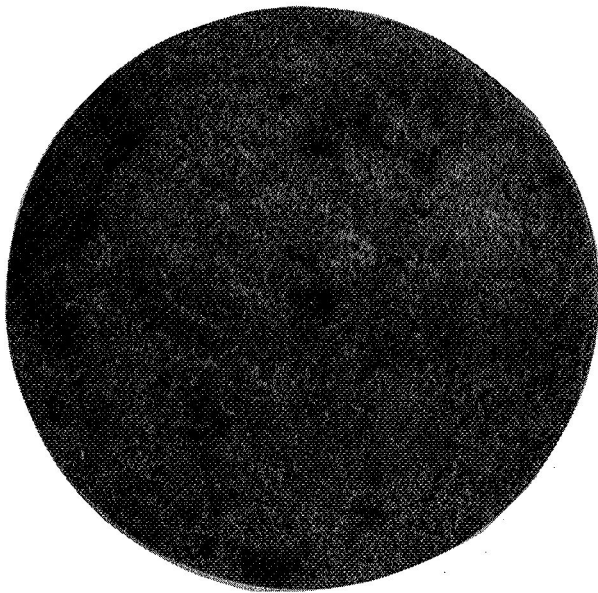
Figure 8. Density of F410 zirconia-W-3% Re wire reinforced composites, isopressed and vacuum sintered at 4000°F for 4 hours.



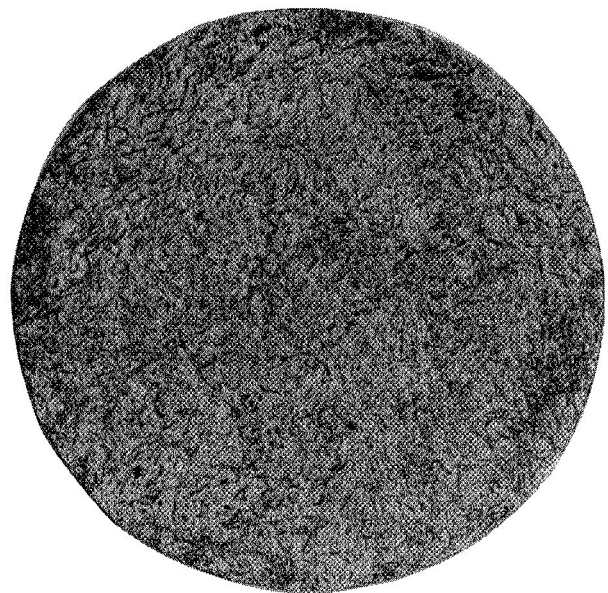
a- 3 v/o



b- 5 v/o

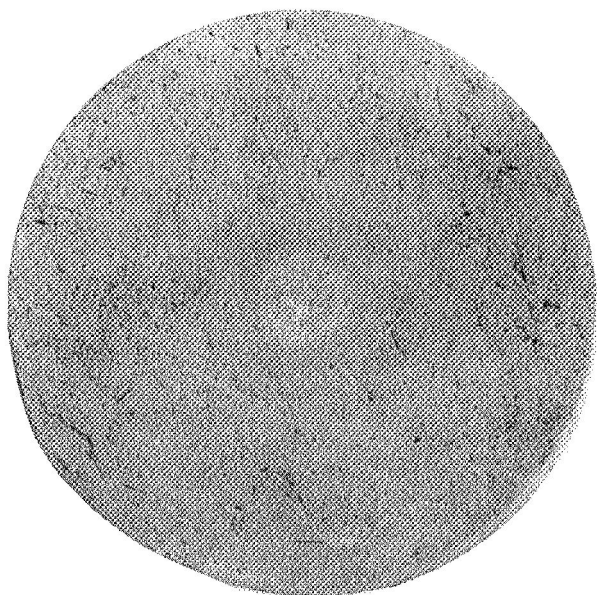


c- 10 v/o



d- 20 v/o

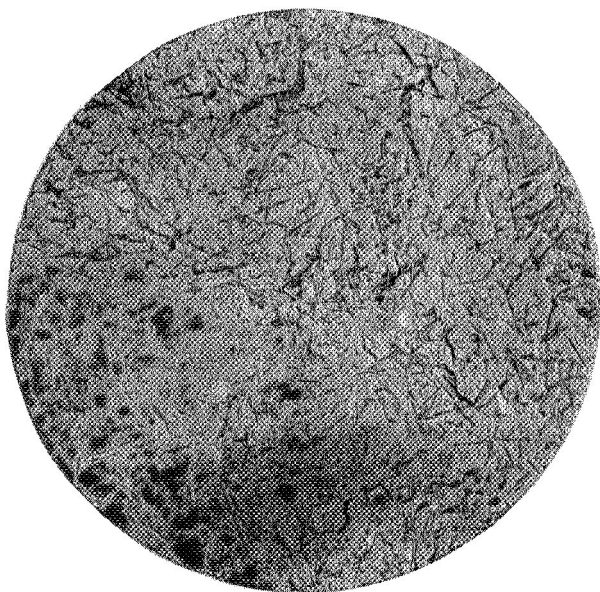
Figure 9. Isopressed and vacuum-sintered composites of F410 zirconia reinforced with various indicated amounts of 2 mil diameter x 1/8" long W-3% Re chopped wire.



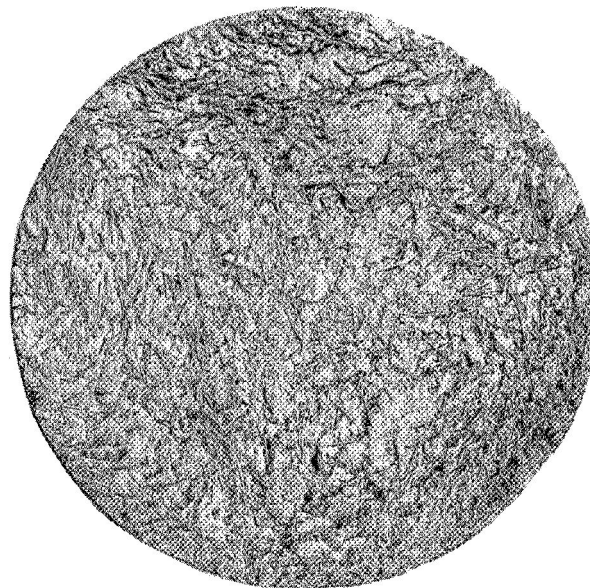
a- 3 v/o



b- 5 v/o



c- 10% v/o



d- 20% v/o

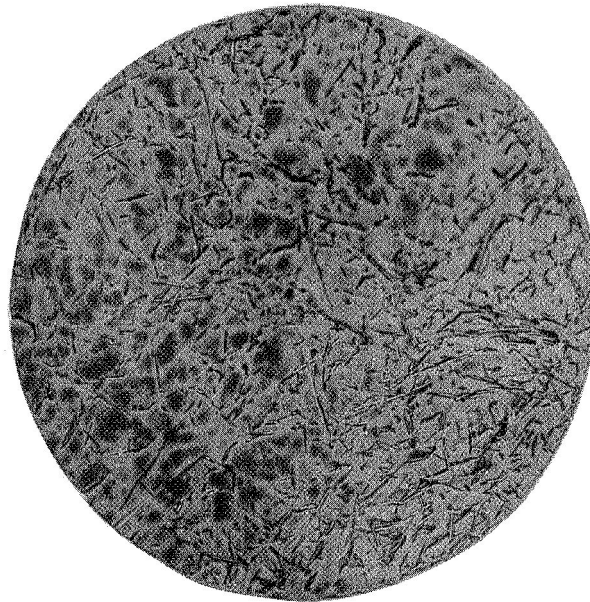
Figure 10. Isopressed and vacuum-sintered composites of F410 zirconia reinforced with the various indicated amounts of 3.5 mil diameter x 3/16" long W-3% Re chopped wire.



a- 3 v/o



b- 5 v/o



c- 10 v/o

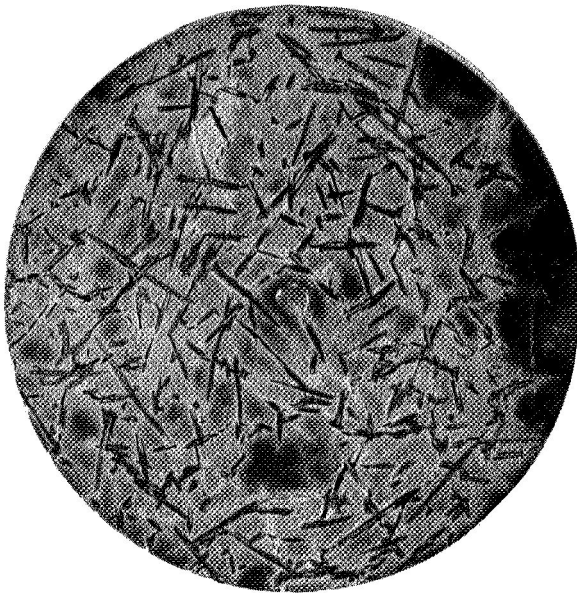
Figure 11. Isopressed and vacuum-sintered composites of F410 zirconia reinforced with the various indicated amounts of 5 mil diameter x 5/16" long W-3% Re chopped wire.



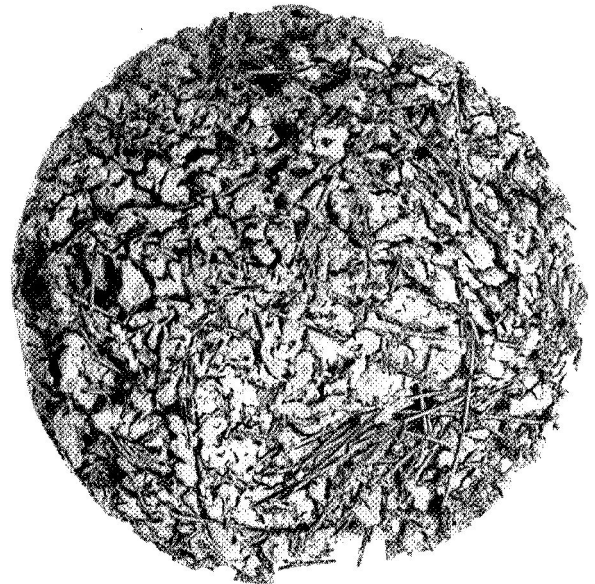
a- 3 v/o



b- 5 v/o



c- 10 v/o



d- 20 v/o

Figure 12. Isopressed and vacuum-sintered composites of F410 zirconia reinforced with the various indicated amounts of 10 mil diameter x 5/8" long W-3% Re chopped wire.

Metallographic examination - Metallography was used to obtain a better understanding of the behavior of these reinforced composites. It was found that the higher porosity associated with higher wire volumes occurs chiefly at the wire interface and in voids formed by clusters of wires. This behavior is evident in the microstructures of a 3 v/o 5-mil reinforced sample compared to a 10 v/o 3.5 mil reinforced sample shown in Figures 13 and 14. In the 3 v/o sample, the pores are distributed uniformly throughout the matrix, and the metal wires appear well-bonded to the matrix. The 10 v/o sample shows similar pores distributed throughout the matrix, but large void spaces also surround the reinforcing fibers. The loss of fiber-matrix bond area represented by such voids would be expected to be detrimental to the performance of such composites.

Petrographic analysis - A petrographic examination of the unreinforced matrix materials and composite structures in the as-sintered condition as well as after thermal shock quench testing was performed by Zircoa. Petrographic analysis is performed on thin polished sections, and viewed by transmitted light, which affords a three-dimensional view of the microstructure. This technique allows the study of phase relationships and the observation of residual stresses in the ceramic. The observations from this technique are easiest to interpret when viewed in full-color. However, some of the more salient features are apparent in black-and-white as illustrated below.

One of the more promising matrix materials for use in this program is a 2.85% MgO-stabilized zirconia. Figure 15 is a polarized light view of an unreinforced sample of this material which had been isopressed and vacuum sintered. This material was 71% cubic as measured by x-ray diffraction and had been sintered to 97% of theoretical density. In the figure, the pores are polygonized due to the 4000°F sintering treatment. Slip bands are evident in the area of the pores. This is seen as deformation bands evident as the symmetrical light streaks emanating from the pores. The fine orthogonal set of striations in the background are slip traces which indicate an overall deformation of the ceramic. This ability to deform by slip helps account for the relatively good thermal shock characteristics of these MgO-stabilized zirconia compositions.

Figure 16 shows a polarized-light view of Zircoa's F410 material, another leading candidate in this program. This material, unreinforced, has been sintered to a density of 90% and is 56% cubic. The amount of porosity appears to be large because the view is through a volume of material and all pores within this volume are visible within the field of view. The sample shows some fine slip within the grains and a little elastic strain. The particular location which was photographed showed a large amount of strain as is evidenced by the bright fringes on the grain in the center. This amount of strain is not typical of the bulk of the sample.

The foregoing matrix materials are typical examples of the unreinforced materials examined in the as-sintered condition. The thermally shocked materials contained no discernable differences from the unshocked materials.

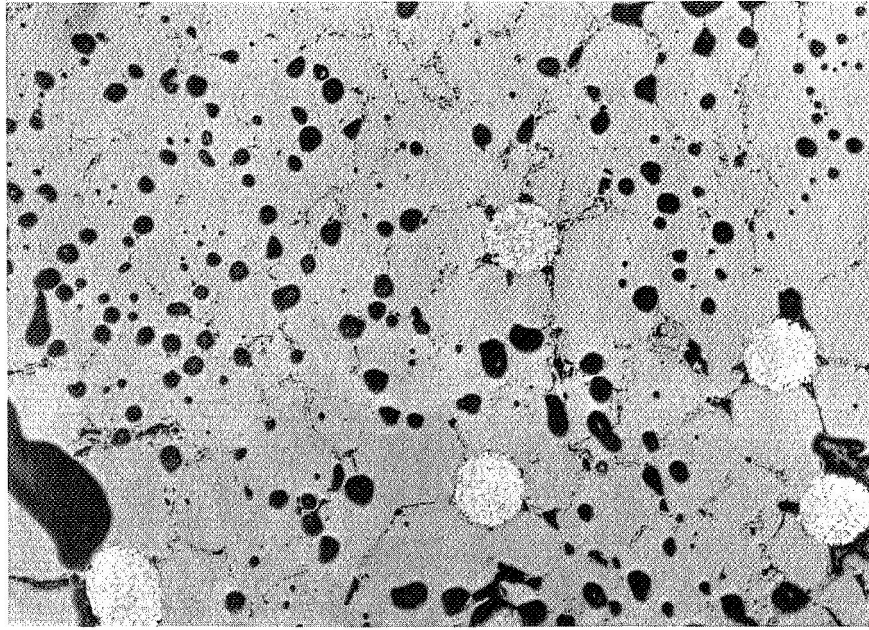


Figure 13. Zirconia matrix reinforced with 3 v/o of 5.0 mil W-3% Re wire. Isopressed and vacuum sintered. 75X magnification.

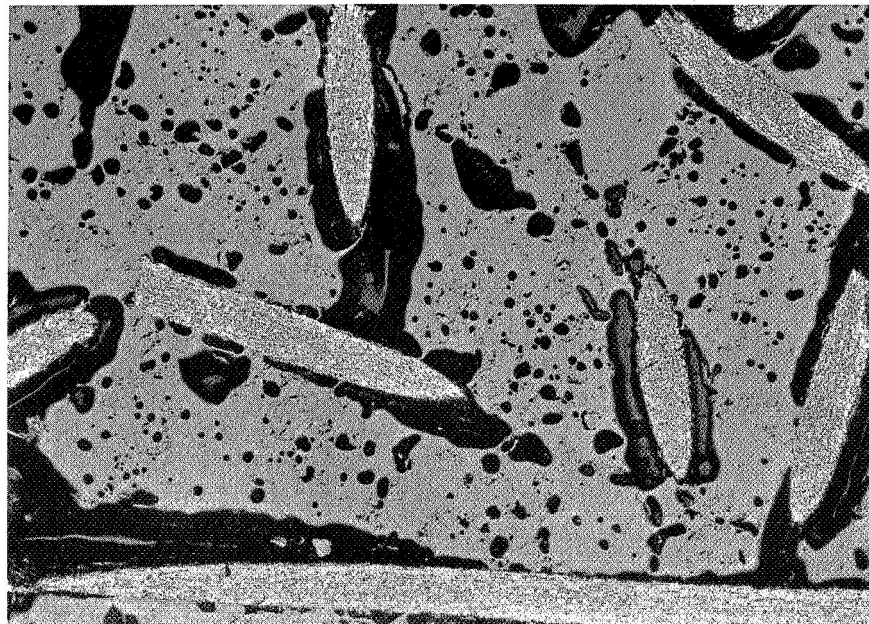


Figure 14. Zirconia matrix reinforced with 10 v/o of 3.5 mil W-3% Re wire. Isopressed and vacuum sintered. 75X magnification.

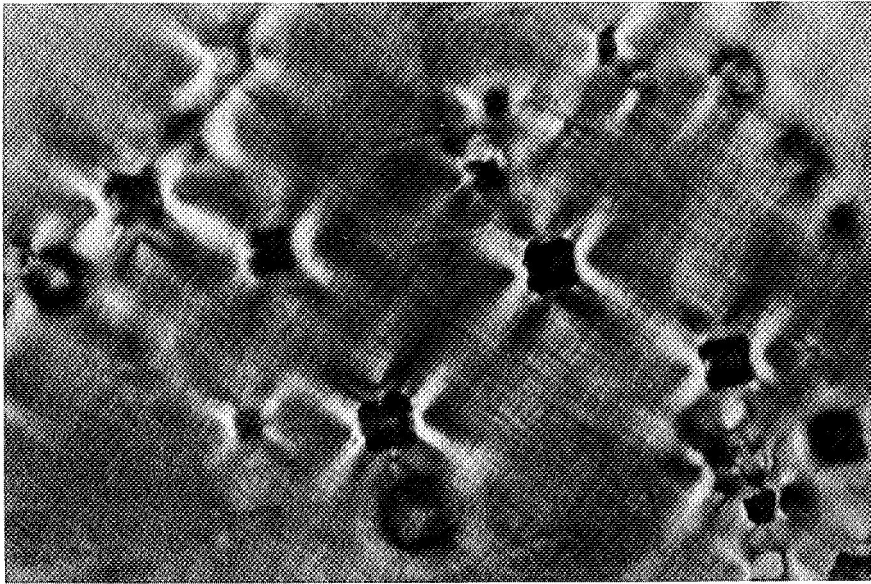


Figure 15. As-sintered unreinforced 2.85% MgO-stabilized zirconia; polarized transmitted light, gypsum plate. 1500X

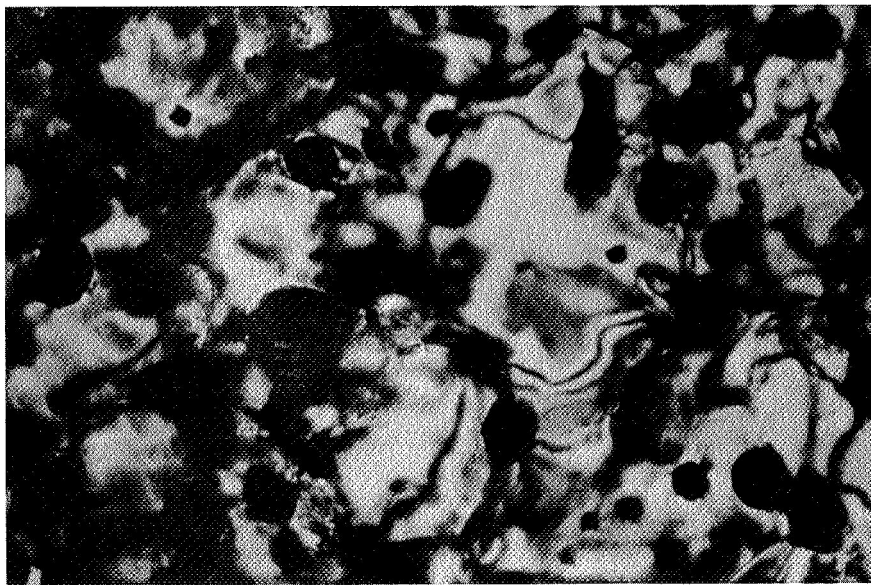


Figure 16. As-sintered unreinforced F410 zirconia; polarized transmitted light. 360X

Petrographic techniques were also used to study the wire-reinforced composites to determine the effect of the reinforcing wires on the zirconia matrix material. A microstructure of F410 zirconia composite containing 10 v/o of 10-mil diameter wire, Figure 17, shows evidence of radial cracking due to mismatch in thermal expansivity between the wire and matrix. The grain size is variable and it is probable that the wires have interfered with grain growth. The sample contains a large amount of porosity and the zirconia grains exhibit a fairly large amount of elastic strain.

Figure 18 is a view of the same matrix material reinforced with 10 v/o of 3.5 mil wire showing photoelastic patterns in the zirconia grains which seem to be clearly associated with stresses arising due to mismatch in thermal expansivity. The figure shows some cracking, but this was noticeably less than in the specimen containing wires of larger diameter.

The analysis of these thermally shocked composites indicates that the higher volume fractions of wire interfere with sintering of the matrix material which results in higher porosity and less bonding of the component materials. Composites containing the 2.0-mil diameter wire exhibited less evidence of residual stress due to the thermal expansivity mismatch of the components than do the composites containing the larger wire diameters.

Transverse rupture properties - Transverse rupture properties were measured by a 3-point bend test on these composites both in the as-sintered condition and after being subjected to a thermal shock quench test. The quench test consisted of a single quench from 1930°F into an ice-brine solution as described more completely in the Task 2 portion of this report. The resultant bend strength measurements are listed in Table 10.

It was desired to obtain as much information as possible from these data concerning optimum wire diameter and content. To do this, it was considered most meaningful to study the strength after the thermal shock quench test since the residual strength would then likely be dependent on the effectiveness of the reinforcing fibers. Accordingly, transverse rupture strengths were plotted as a function of both wire diameter and wire content as shown in Figure 19. These data show that wire contents in the 5-10 v/o range are the most effective. Also, wires with diameters of from 2 to 5 mils give the best reinforcement. It is also indicated that the smaller diameter wires can be effectively used in greater amounts than can the larger diameter wires. For example, at the 20 v/o loading the best results were with the 2-mil diameter wires, while at the 3 v/o loading the best results were with the 10-mil wires. In summary, these results were encouraging in that they indicated definite ranges where optimum reinforcement of composites was obtained. This was a valuable guide to further composite development.

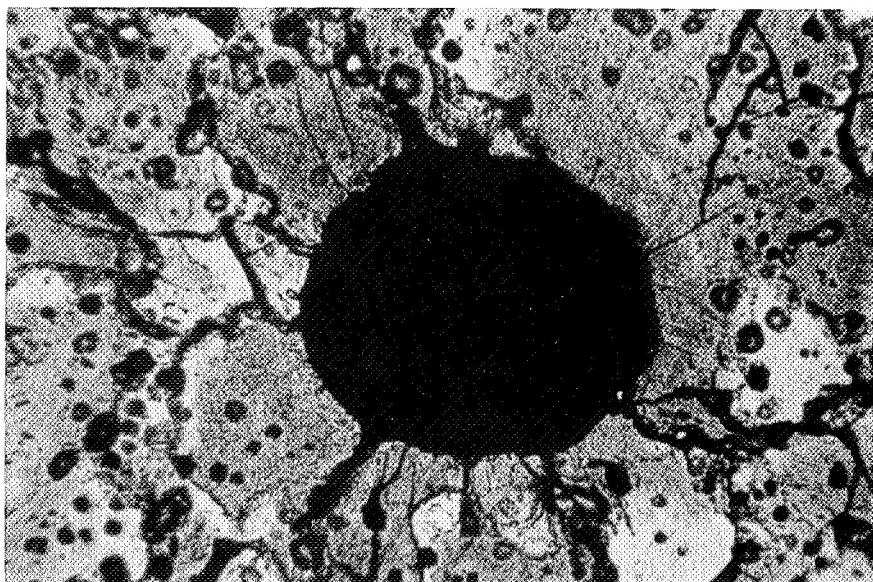


Figure 17. F410 matrix composite reinforced with 10% of 10-mil diameter wire after thermal shock quench testing. Plane transmitted light. 150X

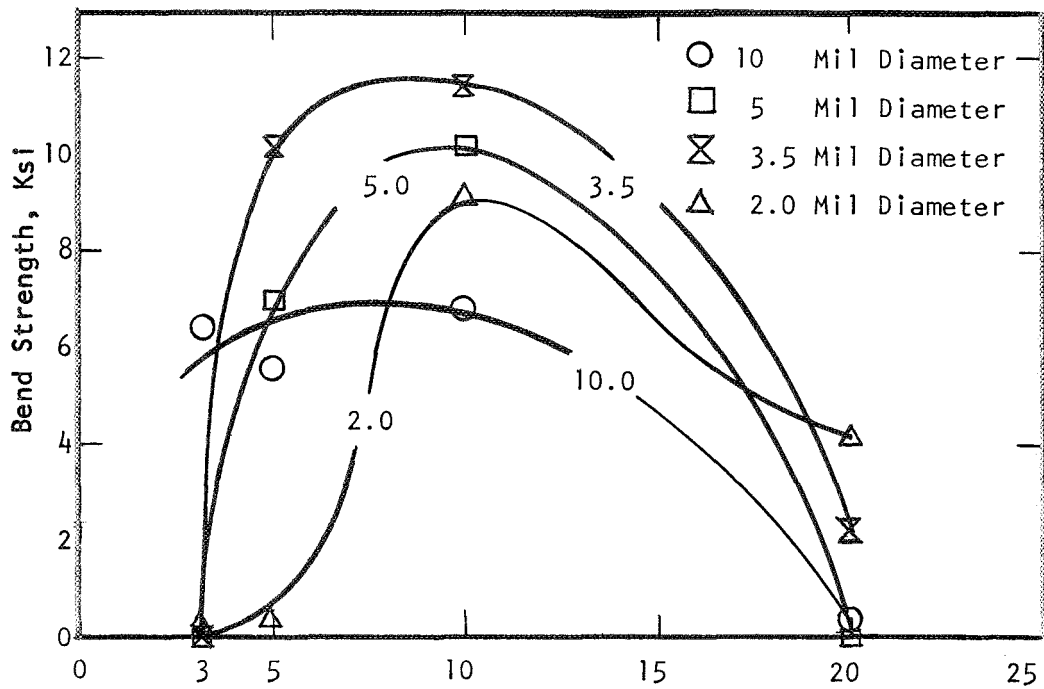


Figure 18. F410 matrix composite reinforced with 10% of 3.5 mil diameter wire after thermal shock quench testing. Polarized transmitted light. 700X

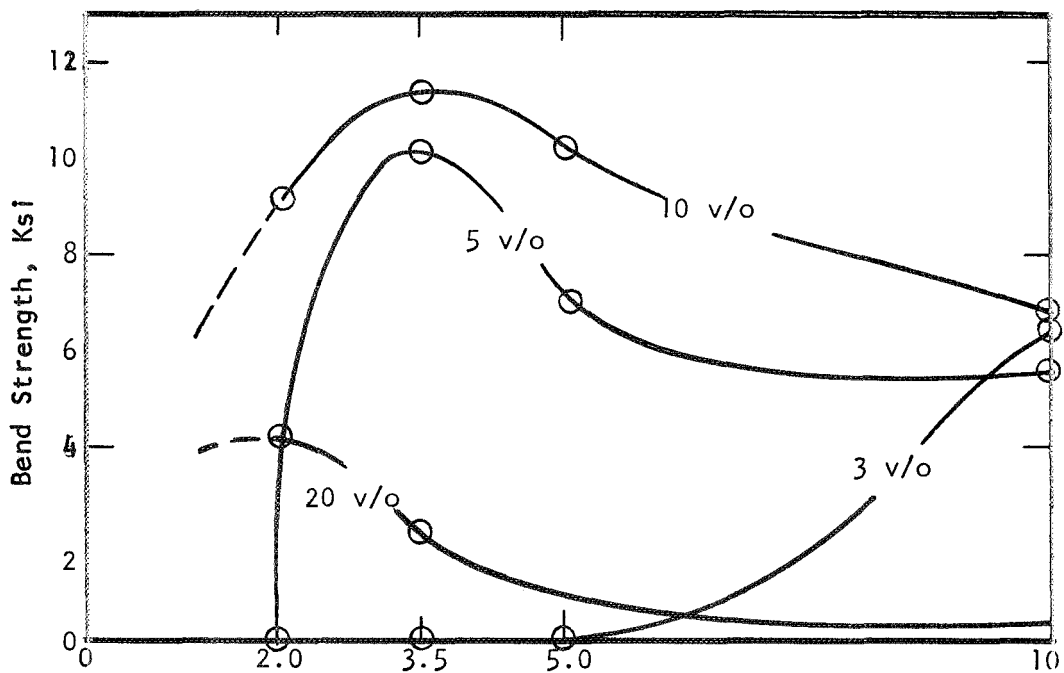
TABLE 10

ISOPRESSED AND VACUUM SINTERED F410 MATRIX COMPOSITES REINFORCED WITH W-3%RE CHOPPED WIRE: ASPECT RATIO OF 63

Wire Diameter Mils	Volume Percent Wire	Porosity %	Bend Strength As Sintered Ksi	Bend Strength After Thermal Shock Ksi	Comments
2.0	3	10	15.7	0	Thermal Shock Failure
2.0	5	8	14.2	0.2	Thermal Shock Failure
2.0	10	15	14.6	9.1	
2.0	20	35	8.1	4.2	
3.5	3	8	20.5	0	Thermal Shock Failure
3.5	5	8	17.3	10.2	
3.5	10	19	9.0	11.4	
3.5	20	40	6.7	2.3	
5.0	3	8	18.5	0	Thermal Shock Failure
5.0	5	9	16.6	7.0	
5.0	10	16	9.7	10.2	
5.0	20	-	-	-	Not Sinterable
10.0	3	9	10.3	6.4	
10.0	5	10	4.7	5.6	
10.0	10	16	5.0	6.8	
10.0	20	56	-	-	Not Machinable



(a) Reinforcement Wire Content, Volume Percent



(b) Reinforcement Wire Diameter, Mils

Figure 19. Bend strength after thermal shock testing as a function of (a) reinforcement wire content and (b) wire diameter. Isopressed and vacuum sintered F410 zirconia-W-3%Re composites.

2. Hot Pressing Studies

As an alternate to the relatively long-time, high-temperature (4 hrs. at 4000°F) processing cycle used for the isopress-and-sinter approach to composite fabrication, the hot-pressing consolidation approach was explored. Both the conventional hot pressing approach and the use of reactive hot pressing (pressing in the temperature range of monoclinic-to-tetragonal phase change for zirconia) were explored in this study.

Conventional hot pressing - The initial hot pressing studies were carried out using unreinforced F410 zirconia with the aim of defining processing cycles required to obtain high density in a zirconia compact. The hot pressing was performed in graphite tooling with a 10-mil thick molybdenum liner in the mold to minimize carbon contamination. The graphite mold, also used as the susceptor, was induction heated by a 100KW, 9600 cps motor generator. The mold assembly was buried in graphite powder inside a quartz tube. No protective atmosphere was used other than that provided by the graphite powder. A pressure of 8000 psi was used for all pressing cycles.

Pressing cycles of 2700°F to 3000°F produced compacts in the 98 to 99% density range. However, a problem of contamination from the graphite tooling was encountered despite the use of the molybdenum protective liner. The use of high density alumina liners and punches eliminated the contamination problem, but the alumina punches failed at pressures approaching 8000 psi. Because of this limitation and tooling fabrication difficulties, the use of ceramic tooling was abandoned.

Reactive hot pressing - In order to overcome the carbon contamination and ceramic tooling problems associated with conventional hot pressing, hot pressing in the 1900-2300°F temperature range using reactive heating cycles was employed. The reactive cycle involves thermal cycling of the sample, while under pressure, through the monoclinic-to-tetragonal phase change to take advantage of the increased reactivity of zirconia while undergoing the phase change.

A series of composites containing 5 v/o of 3.5 mil diameter reinforcing wire were hot pressed by this technique. Various matrix materials were used. Most of these consisted of monoclinic zirconia blended with CeO_2 and Y_2O_3 as stabilizers. The compacts, in graphite tooling, were brought up to 1900°F and then 8000 psi pressure was applied. Temperature was then raised to 2300°F in 15 minutes and allowed to cool to 1900°F in 15 minutes under full pressure. Two specimens of each material composition were fabricated. The first set of specimens were subjected to a single cycle thermal shock quench from 1930°F in the as-pressed condition. The second series of specimens were vacuum sintered for 4 hours at 4000°F before thermal shock testing. Data derived from these specimens are presented in Table 11.

The data indicate that density of hot pressed compacts is somewhat dependent on the degree of stabilization of the matrix. The highest densities 94 to 97%, were attained by the 6% Ti composition which is completely monoclinic. Pressings of the F410 material, which is prestabilized at approximately 60% cubic, reached a maximum of 69% of theoretical density. This effect of degree of stabilized cubic phase detracting from the effectiveness of the reactive hot pressing cycle is shown in Figure 20.

TABLE 11

REACTIVE HOT PRESSED ZIRCONIA COMPOSITES REINFORCED WITH 5 v/o OF 3.5 MIL DIAMETER W-3% Re WIRE

Matrix Material	Density As-Pressed g/cc	% Theo.	Test Condition	Sintered Density g/cc	% Theo.	Quench Test Thermal Shock Behavior	Bend Strength psi	Comments on Microstructure
3% Y ₂ O ₃	5.77	91	As Hot Pressed	-	-	Sound	5,000	Microcracks present
3% Y ₂ O ₃	5.76	91	Vacuum Sintered			Sound		
5% Y ₂ O ₃	4.58	73	As Hot Pressed	-	-	Sound	7,200	No visible microcrack
5% Y ₂ O ₃	5.29	83	Vacuum Sintered	5.55	88	-	-	Cracked in Sintering
5% CeO ₂	6.07	96	As Hot Pressed	-	-	Sound	6,800	Microcracks visible
5% CeO ₂	6.03	95	Vacuum Sintered	5.62	89	Sound		
10% CeO ₂	5.20	82	As Hot Pressed	-	-	Sound	9,700	No visible microcrack
10% CeO ₂	6.15	97	Vacuum Sintered	5.62	89	Failed	-	
6% Ti	5.93	94	As Hot Pressed	-	-	Sound	13,100	No visible microcrack
6% Ti	6.17	97	Vacuum Sintered	5.52	87	Sound		
F410	4.35	69	Vacuum Sintered	6.02	95	-	-	Cracked in Sintering

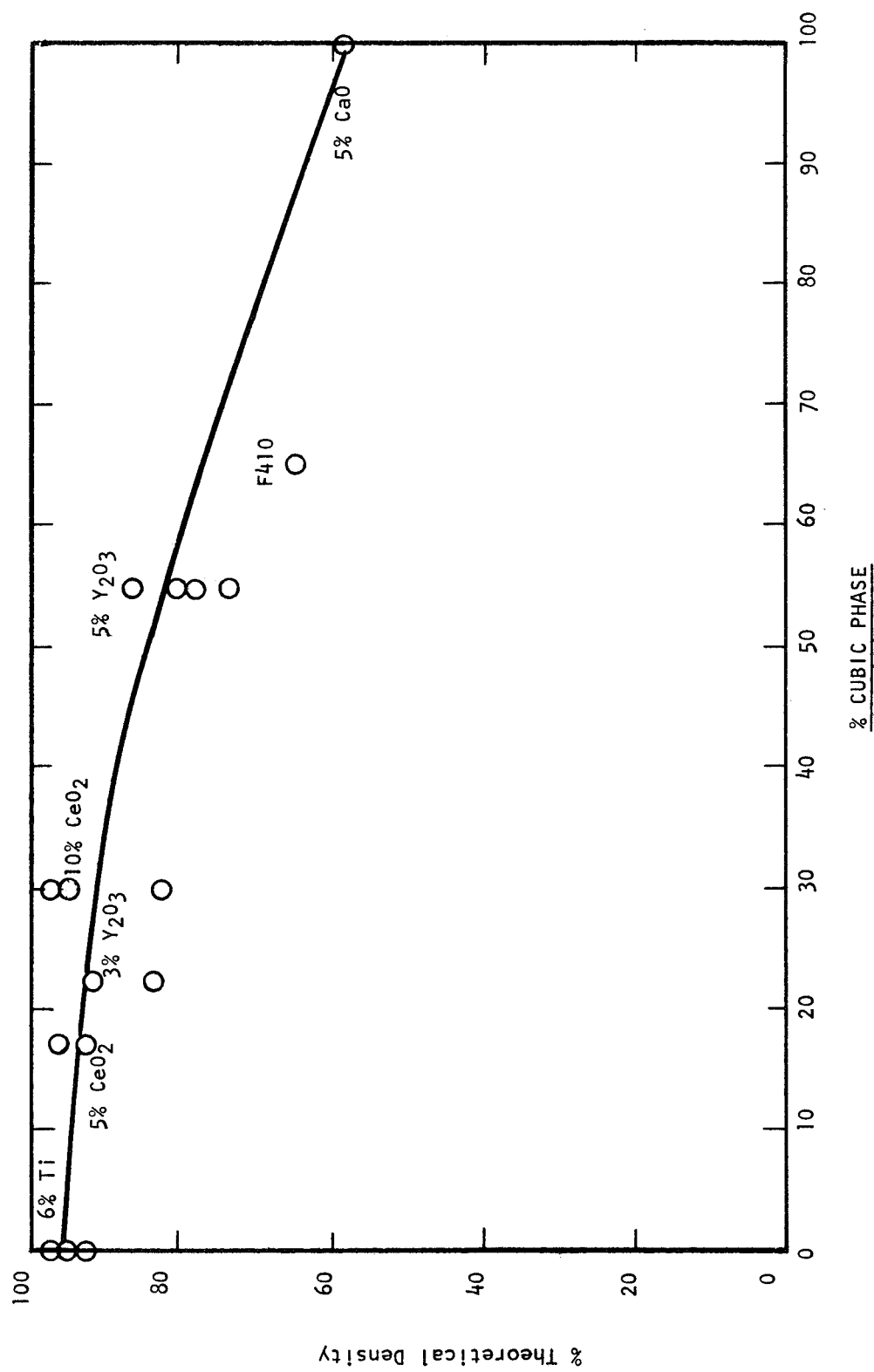


Figure 20. Reactive hot pressed zirconia composites reinforced with 5 v/o of 3.5 mil diameter W-3%Re wire showing effect of cubic phase on the resultant density of the compacts.

Attempts to improve the hot-pressed densities by a vacuum sintering cycle proved ineffective. Most of the vacuum-sintered compacts had a lower density after sintering. The lower density was caused by extensive microcrack formation presumably due to the thermal expansivity mismatch of the component materials. The F410 composite which did densify during sintering was too badly cracked to be useable.

The same reactive hot pressing cycle was applied to larger pressings but produced densities only on the order of 75 to 85% of theoretical. These larger specimens, 1-1/2 inch OD x 1/2 inch ID x 3/4 inch long, were produced for thermal shock testing by a plasma jet test. The lower pressed densities are probably due to increased die wall friction resulting from the increased surface area of this type of specimen geometry. It was necessary, therefore, to raise the processing temperature to 2500°F in order to reach an acceptable pressed density on the larger compacts. Densities of 92-95% of theoretical were obtained with this higher temperature cycle.

The reactive hot pressing cycle is applicable to monoclinic zirconia and to compositions compounded by mechanical mixtures of monoclinic zirconia and a stabilizing agent. Prestabilized powders (materials that are fully or partially stabilized as a result of previous thermal treatments) do not respond to the reactive hot pressing cycle. As a consequence, it was necessary to use conventional higher temperature cycles to hot press F410 matrix composite materials. A density of 6.3 g/cc (99%) for an F410 matrix - 5 v/o W-3% Re wire composite was achieved by a 10-minute, 2800°F, 8000 psi cycle.

Hot pressing is capable of producing a high density zirconia composite at relatively low processing temperature, a condition which helps to retain most of the original properties of the reinforcing wires. Additionally, compacts can be hot pressed with good dimensional control. This is an important factor in reducing the costly diamond grinding necessary to produce composite hardware. The performance of the hot pressed composites however, as discussed under the Task 2 section of this report, is apparently inferior to that of the isopressed and vacuum-sintered composites. Hot pressing, therefore, was not used to produce any of the hardware evaluated in the subsequent parts of this program.

3. Selected Fabrication Techniques

Except for those specimens prepared by hot pressing as discussed above, an isopress-and-vacuum-sinter procedure was used for composite fabrication. This procedure consists of mixing the zirconia powder and chopped fibers in a powder blender until a homogeneous mixture is obtained. This is often a difficult step because the wires tend to form tangled agglomerates, particularly at the higher wire contents and with the longer lengths of chopped wire. A twin cone powder blender with a high speed intensifier bar was found helpful in achieving homogeneity in these powder-wire mixtures.

The next step involves the loading of the mixed composite into a rubber membrane mold. The metal wires tend to form a skeletal structure of a low bulk density, so tamping of the loose-filled mold is often required. The mold is then sealed and placed inside a liquid filled pressure chamber in which the pressure is raised to the desired pressing condition - 30,000 psi for this program. The isostatic pressure present in the chamber helps insure uniform compaction throughout the sample. After pressing is complete, the rubber membrane mold is removed from the sample in preparation for sintering.

Vacuum sintering was used in this program to protect the reinforcing wires from oxidation. A sintering temperature of 4000°F was deemed suitable for these composites based on prior experience. To help control thermal stresses within the composite during sintering, a 16-hour heat up cycle to 4000°F and a 8-hour cool-down cycle was used with a 4-hour hold at the sintering temperature.

The aspect ratio of the reinforcing wire was maintained at about 60 (it actually varied from 54 for the 3.5 mil x 3/16" wire to 63 for the 2, 5, and 10 mil wire). The effect of aspect ratio of the wires was studied in Task 3 of the program where it will be discussed in detail. This study showed that 60 was fortunately a good choice of wire aspect ratio and was, therefore, used throughout the program.

Using the W-3% Re reinforcing wire combined in various sizes and amounts with the more promising matrix materials discussed earlier in this report, composite specimens were made by the isopress and sinter method discussed above. Wire reinforcement parameters were varied in the 5-10 v/o range and in the 2-10 mil diameter range as had been determined (and discussed earlier in this report) to produce the optimum composites.

These composites were then evaluated by thermal shock tests with the aim of choosing the best ones for further evaluation in the program. The various composites produced and tested are detailed in the Task 2 discussion together with the corresponding thermal shock results and rationale for selection or rejection of the composites to be considered for rocket nozzle fabrication.

TASK 2 - THERMAL SHOCK TESTS

The primary aim of reinforcing ceramic structures for rocket nozzle applications is to improve their thermal shock characteristics. Therefore, it is fitting that thermal shock behavior be one of the primary criteria on which to choose an optimum reinforced zirconia composite. The approach in this program was to find a number of matrix materials which possessed inherently good thermal shock resistance in the unreinforced condition and then combine these with the optimum reinforcing material in such a way so as to yield the optimum composite structure.

To satisfy the range of requirements imposed by this approach, three types of thermal shock tests were employed. These included a quench test, a plasma-jet test, and an electron beam test.

A. Quench Tests

The quench test was used to define the temperature differential (ΔT) required to cause failure of a test specimen. This test was primarily used to rate zirconia matrix materials in the unreinforced condition. The quench test was also used for preliminary evaluation of materials composited with various fiber amounts and geometry by means of a single quench cycle from the maximum temperature.

1. Experimental Procedure

The quench test used a disc specimen 1.5 inches in diameter x 1/4 inch thick insulated on the ends to limit heat flow to the radial direction. Specimens were clamped in a test fixture as illustrated in Figure 21, furnace heated to the desired temperature, and quickly quenched into an ice-brine solution at about 30°F. Failure of the specimen was defined as complete cracking in the fixture or by subsequent light manual flexing. An argon atmosphere was used in the furnace to prevent oxidation of the reinforcing wires.

To measure the ΔT value of a material by this test usually required 3 to 4 specimens. The testing was started at a temperature below the failure point of the material and taken through successive quenches, increasing the temperature 50°F for each succeeding quench until the specimen failed. The next specimen was started at the last temperature below failure and the cycles repeated until failure. The process was repeated until a specimen failed in two quench cycles. The ΔT was defined as the average value of the last two temperatures.

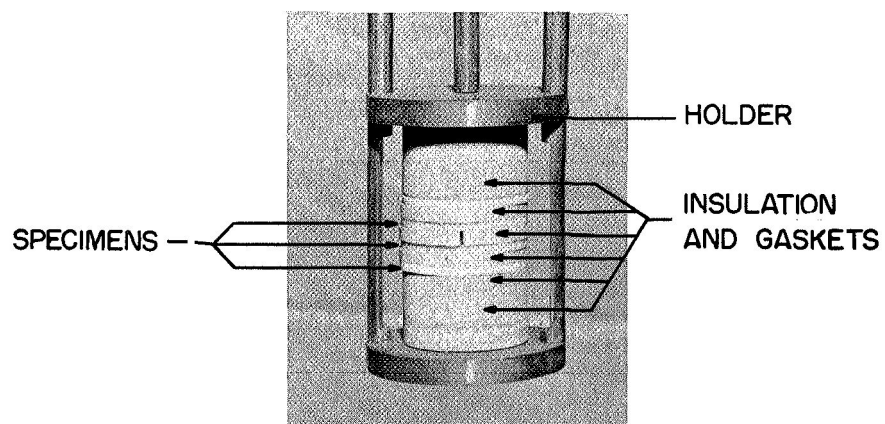


Figure 21. Close-up of clamping device for holding test specimens in thermal shock quench test apparatus.

2. Results of Quench Tests

All candidate zirconia matrix materials were screened in the unreinforced condition by means of this quench test. For the purposes of discussion, these materials may be categorized as follows:

1. Commercially available off-the-shelf materials.
2. Custom stabilized compositions formulated by Zircoa employing MgO and CaO stabilizers and prepared in three ranges of particle sizes.
3. Various stabilizer systems also compounded by Zircoa using various amounts and types of stabilizers.
4. Various stabilizer systems compounded by TRW by employing a single step process combining stabilization with the sintering operation.

Commercially-available materials - The thermal shock properties of off-the-shelf zirconia materials are shown in Table 12. The data show that thermal shock resistance is dependent on stabilization with 100% cubic compositions having low ΔT values. Partially-stabilized materials have a much greater resistance to thermal shock failure attributed to their lower thermal expansivity compared to the fully-stabilized material.

Custom MgO and CaO formulations by Zircoa - Data derived from the series of custom-stabilized materials formulated by Zircoa are tabulated in Table 13. This series of compositions again shows a requirement for a partially stabilized matrix to achieve a maximum ΔT value. The range of powder particle sizes have not had much influence on the thermal shock resistance of the sintered material.

During the course of thermal shock testing, a number of materials were found to have ΔT values above 1000°F. Consequently, 800°F was established as a cut-off point in subsequent testing and no ΔT values were established for materials that failed in a single quench cycle from 800°F.

Other Zircoa-prepared compounds - Thermal shock results of the other eight zirconia compositions prepared by Zircoa are listed in Table 14. The best material and the only one of further interest was the 10% CeO₂ stabilized material which contained 28% of the stabilized phase (tetragonal rather than cubic for CeO₂-stabilized material).

TRW-prepared compositions - The quench test results of these compounds are shown in Table 15. Of these 12 compositions, two of the Y₂O₃ and two of the CeO₂ stabilized systems showed promise. Again, partial stabilization was seen to promote thermal shock resistance in these compounds.

TABLE 12

THERMAL SHOCK BEHAVIOR OF OFF-THE-SHELF ZIRCONIA MATRIX MATERIALS

Stabilizer Composition	Vendor	% Cubic	% Porosity As-Sintered	ΔT ($^{\circ}F$)
3% CaO	Zircoa	52	8	$\approx$ 550
5% CaO	Zircoa	95	9	325
3% MgO	Zircoa	60	5	$\approx$ 850
4% MgO	Harbison-Walker	68	10	$\approx$ 450
6% MgO	Zircoa	100	11	325
F410	Zircoa	56	10	1075
12% Y ₂ O ₃	Zircoa	100	11	275
8% Y ₂ O ₃	Zircoa	92	15	325
6% Ti	Consolidated Astronautics	0	9	1225
3% B ₂ O ₃	Consolidated Astronautics	0	15	Unsuitable

TABLE 13

THERMAL SHOCK BEHAVIOR OF MgO-CaO STABILIZER SYSTEMS PREPARED BY ZIRCOA

<u>Stabilizer</u>	<u>Texture</u>	<u>% Cubic</u>	<u>% Porosity As-Sintered</u>	<u>ΔT ($^{\circ}F$)</u>
2.65% MgO	Coarse	69	7	$\approx$ 600
	Medium	72	6	$\approx$ 700
	Fine	62	2	1025
2.85% MgO	Coarse	78	10	$<$ 800
	Medium	76	9	850
	Fine	71	3	$<$ 800
3.05 MgO	Coarse	83	8	$\approx$ 500
	Medium	83	7	$<$ 800
	Fine	77	4	$<$ 800
CaO Modified	Coarse	86	6	$<$ 800
	Medium	85	6	$<$ 800
	Fine	87	2	$<$ 800

TABLE 14

THERMAL SHOCK BEHAVIOR OF ZIRCONIA WITH VARIOUS STABILIZER SYSTEMS PREPARED BY ZIRCO

<u>Stabilizer Composition</u>	<u>% Cubic</u>	<u>% Porosity As-Sintered</u>	<u>ΔT (°F)</u>
6% Y_2O_3	95	2	< 800
8% Y_2O_3	100	2	< 800
15% Mixed Rare Earths	87	10	< 800
25% Mixed Rare Earths	-	10	Unsinterable
10% CeO_2	28 *	10	1075
20% CeO_2	57 *	17	< 800
CaO Modified	-	10	Unsinterable
Y_2O_3 Modified	100	4	< 800

* The stabilized phase in the CeO_2 system is a tetragonal rather than a cubic structure

TABLE 15

THERMAL SHOCK RESULTS OF ZIRCONIA WITH VARIOUS STABILIZER SYSTEMS PREPARED BY TRW

Compositions	Blend	% Cubic As-Sintered	% Porosity As-Sintered	ΔT ($^{\circ}F$)
3% MgO-0.5% CaO	Monoclinic + Cubic	76	7	< 800
4% MgO-0.5% CaO	Monoclinic + Cubic	100	9	< 800
3% MgO-1.0% CaO	Monoclinic + Cubic	100	8	< 800
4% MgO-1.0% CaO	Monoclinic + Cubic	100	10	< 800
3% MgO-2.0% CaO	Monoclinic + Cubic	100	10	< 800
4% MgO-2.0% CaO	Monoclinic + Cubic	100	10	< 800
3% MgO	Monoclinic + MgO	-	9	Unsinterable
6% Y ₂ O ₃	Monoclinic + Y ₂ O ₃	-	7	Unsinterable
5% Y ₂ O ₃	Monoclinic + Cubic	56	7	875
3% Y ₂ O ₃	Monoclinic + Cubic	23	4	1275
10% CeO ₂	Monoclinic + CeO ₂	35 *	10	1075
5% CeO ₂	Monoclinic + CeO ₂	15 *	6	1025

* Tetragonal

3. Selection of Promising Matrix Materials

Based on the above thermal shock testing, density, and sinterability information, the following zirconia materials were selected for further evaluation:

a. Commercially-available materials:

- | | |
|--------------------------------------|-----------------------------------|
| 1. 3% MgO - Zircoa | $\Delta T = 850^{\circ}\text{F}$ |
| 2. F410 - Zircoa | $\Delta T = 1075^{\circ}\text{F}$ |
| 3. 6% Ti - Consolidated Astronautics | $\Delta T = 1225^{\circ}\text{F}$ |

b. Zircoa's specially prepared compounds:

- | | |
|---------------------------------------|-----------------------------------|
| 1. 2.65% MgO Stabilized, fine texture | $\Delta T = 1025^{\circ}\text{F}$ |
| 2. 2.85% MgO Stabilized, med. texture | $\Delta T = 850^{\circ}\text{F}$ |

c. Single step compounds prepared at TRW:

- | | |
|------------------------------|-----------------------------------|
| 1. 3% Y_2O_3 | $\Delta T = 1275^{\circ}\text{F}$ |
| 2. 5% Y_2O_3 | $\Delta T = 875^{\circ}\text{F}$ |
| 3. 5% CeO_2 | $\Delta T = 1025^{\circ}\text{F}$ |
| 4. 10% CeO_2 | $\Delta T = 1075^{\circ}\text{F}$ |

These nine matrix materials were composited with various combinations of the W-3% Re reinforcement wire for evaluation as composite structures by various means including the more severe thermal shock test using a plasma jet heat source described in the following section of this report.

One other set of thermal shock quench tests was performed. This was the testing of a composite structure of F410 zirconia matrix reinforced with various amounts and sizes of reinforcing wire to assess these reinforcing variables. The tests consisted of a single quench into ice brine from 1930°F which is about the upper temperature limit of this apparatus. The thermal shock data together with strength data on these composites have already been discussed in the Task 1 part of this report (see Table 10) and will not be repeated here. The fact that nearly all of these composite specimens survived this quench, however, helped to emphasize the need for a more severe thermal shock test for the discriminating evaluation of reinforced zirconia structures.

B. Plasma Jet Tests

The plasma jet thermal shock tests were performed on a variety of reinforced composite samples in order to evaluate matrix materials, wire reinforcement variables, and to differentiate between pressed-and-sintered and hot-pressed composites.

1. Testing Procedure

This test, shown schematically in Figure 22, used a hollow cylindrical type specimen 1.5" O.D. x 1/2" I.D. x 3/4" long heated on the I.D. by a plasma torch. The specimen was thermally insulated on the top and bottom and water-cooled on the O.D. to induce a temperature gradient of approximately 4500°F across the specimen. The water-cooled jacket on the specimen O.D. was fitted so that no significant structural support was given to the specimen. This test arrangement was designed to result in a tensile hoop stress on the O.D. of the specimen in much the same way that a rocket nozzle is thermally stressed during the initial heat-up portion of its firing cycle.

A time cycle of 3 minutes of continuous heating was used in these plasma jet tests. After each heating cycle, the specimens were cooled to room temperature and examined for signs of cracking or deterioration. Failure of the specimen was defined as the formation of one or more macrocracks on the O.D. surface or complete fracture of the specimen. Specimens were rated by visual appearance for craze cracking, spalling, and signs of melting as well as the number of cycles to failure. A maximum of 8 cycles were run on each specimen unless failure occurred earlier.

There were various types of cracks noted in these test specimens. Craze cracking was the term used to describe cracks in the matrix that did not appear to involve failure of the fibers. This type of cracking does not adversely affect the thermal shock resistance of the composite although it may increase the oxidation rate of the reinforcing fibers. Macrocracks were defined as large, open cracks involving failure of the fibers and loss of structural integrity of the composite. Fissures were cracks formed during the sintering or hot pressing cycle resulting from high fiber concentrations or poor fiber matrix bonding. This type of defect could conceivably propagate and/or allow excessive fiber oxidation.

The initial test was monitored by thermocouples at the O.D., at the I.D. and at a point midway through the specimen wall. Thermocouples were spaced 30° apart on a radial plane through the midpoint of the specimen. The specimen was an isopressed-and-vacuum-sintered composite of an F410 matrix reinforced with 5 v/o of 3.5 mil diameter W-3%Re wire. The heat flux from the plasma jet torch resulting from a power input of 20 KW was sufficiently high to cause considerable melting of the I.D. of the specimen and destroy the thermocouple. A maximum temperature of 135°F was recorded at the O.D. and the mid-point temperature reached a maximum of 1600°F after 30 seconds.

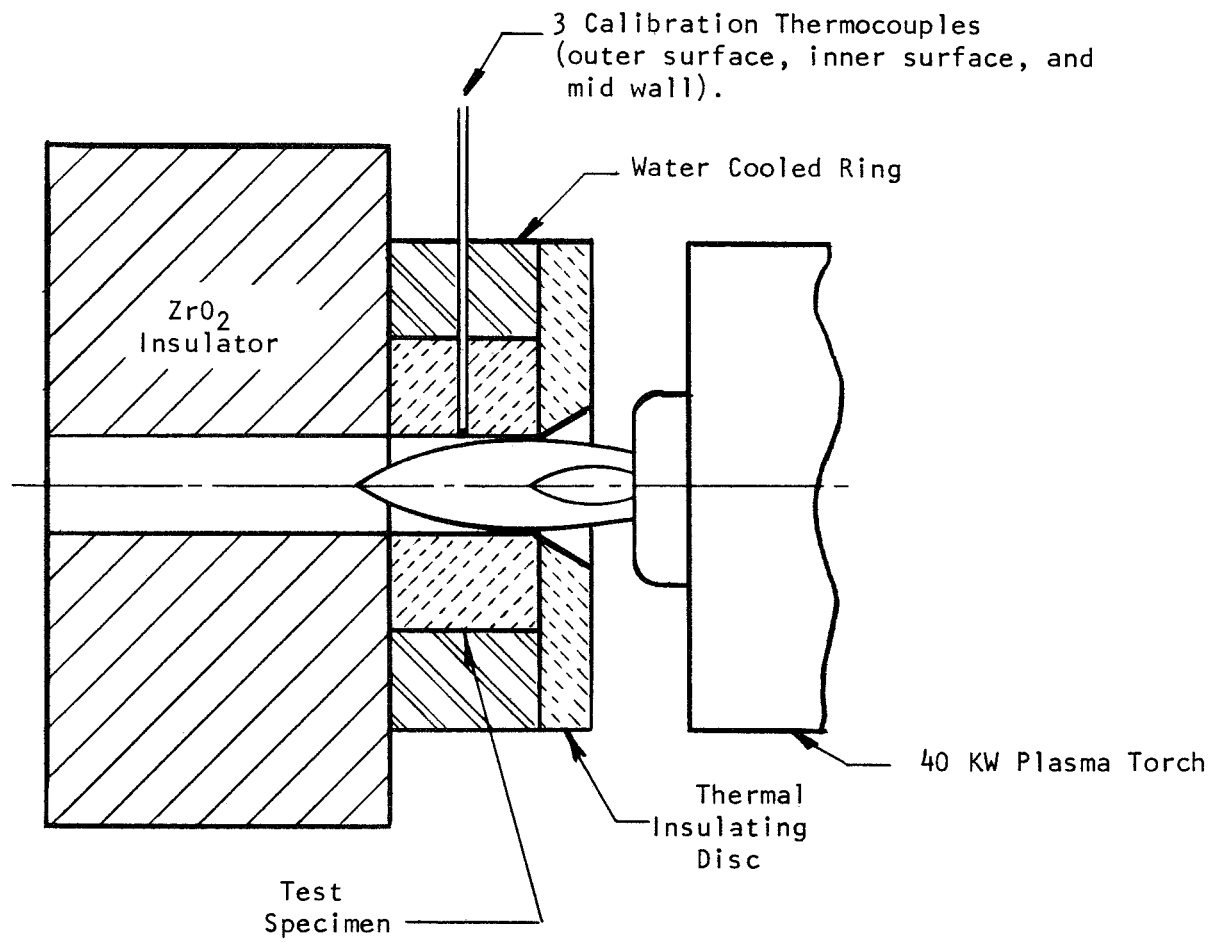


Figure 22. Plasma Jet Thermal Shock Evaluation Rig

This specimen, shown in Figure 23, however, showed no signs of degradation or cracking at the O.D. surface as a result of the test even though the temperature gradient across the specimen was in excess of 4700°F. The heat input to the specimen was lowered by using a 16KW setting of the plasma gun. This power input was just sufficient to cause a slight glazing of the I.D. surface of the F410 matrix specimen.

A second F410 W-3% Re composite specimen was then tested for a 3-minute cycle with a 16KW input from the torch. The thermocouple at the O.D. of this specimen showed a gradual rise in temperature from 36°F at the start of the cycle to 105°F at the conclusion. The temperature at the midpoint of the specimen showed a gradual increase from 36°F at the start to 1450°F at the conclusion of the test.

The thermocouple used to monitor the I.D. surface was composed of W-5% Re and W-26% Re wires. The sensing tip was formed of thermocouple wires flattened to 1-mil thickness and insulated from each other by a 0.2-mil thickness of sheet mica. The sandwich of wires and mica were swaged in a tantalum sheath using ZrO₂ as the insulator. The hot junction was formed by abrading the tip thus bridging the insulation and forming microscopic hot junctions. The thermocouple gave a maximum indicated temperature of 3000°F during the plasma jet test despite the fact that the I.D. surface of the specimen showed definite signs of melting and thus indicating surface temperatures above 4700°F. Examination of the thermocouple at the conclusion of the test showed that the mica insulation had eroded or burned away to a depth of at least 1/8 inch below the sensing tip and thus was not representing the surface temperature. Therefore, it is expected that the surface of the specimen did, in fact, attain about 4700°F during this test.

It was considered that these conditions resulted in the most severe thermal shock tests available with this method, so a plasma jet setting of 16KW was used for all subsequent testing.

2. Matrix Material Evaluation Tests

A series of 12 reinforced composite specimens designed to evaluate matrix materials were fabricated by isopressing and vacuum sintering. These composites were all reinforced by 5 v/o 3.5 mil diameter x 3/16 long wire. None of these vacuum-sintered composites could be broken in a single thermal shock cycle, so it was necessary to run multiple 3-minute cycles. The results of these tests are summarized in Table 16 which also includes the results of other series of plasma-jet tests which will be discussed in subsequent sections of this report.

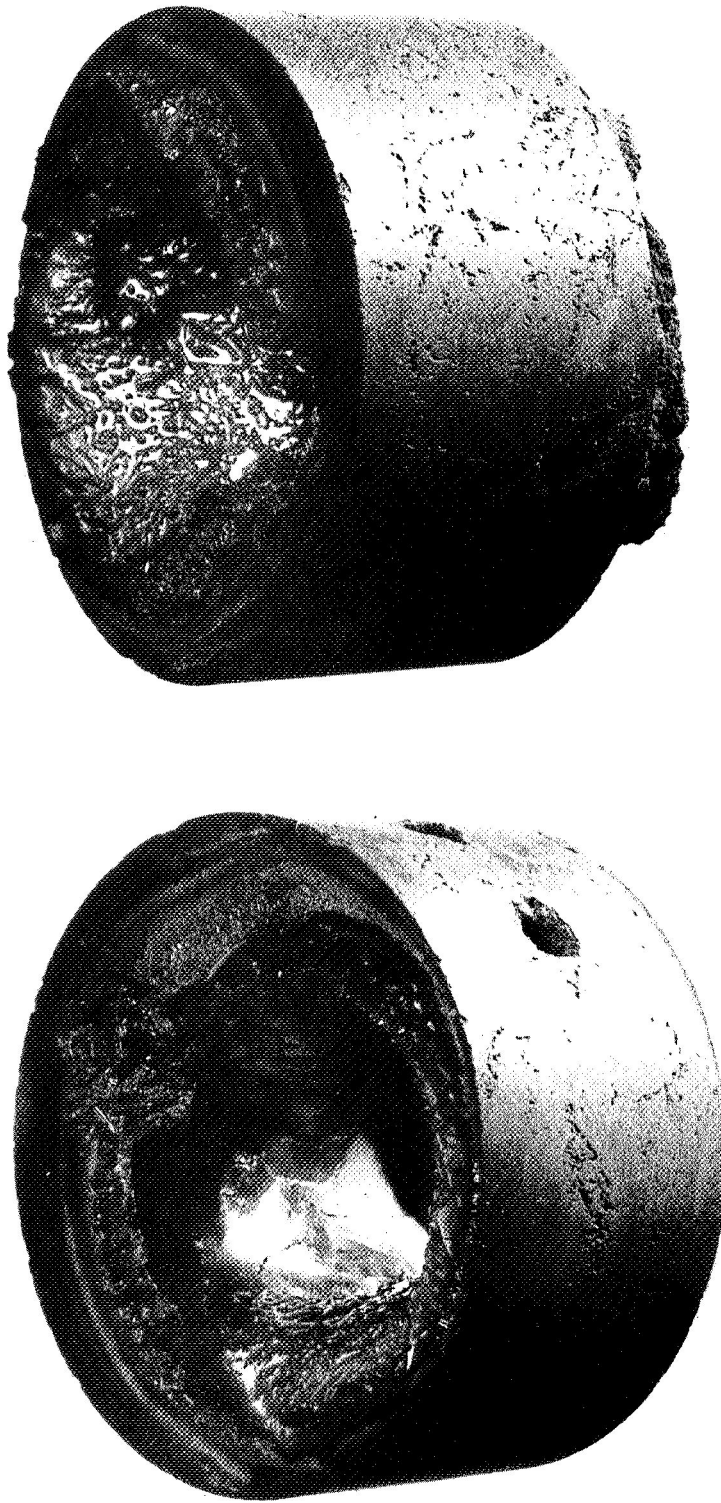


Figure 23. Photograph of first specimen (F410 matrix with 5 v/o of 3.5 mil W-3% Re wire) subjected to the plasma jet thermal shock tests. Approximately 2X.

TABLE 16

PLASMA JET THERMAL SHOCK TESTING OF ISOPRESSED AND VACUUM-SINTERED ZIRCONIA
COMPOSITES REINFORCED WITH W-3%Re WIRE

Matrix Material	Wire		Density g/cc	*Porosity %	Therm. Shock Test Cycles	Visual Appraisal	Melting	Comments
	dia. mils	Vol %						
2.85% MgO-Fine	3.5	5	5.7	10	8	Excellent	Glazed	No Failure
6% Y ₂ O ₃	3.5	5	5.7	10	8	Poor	No Sign	No Failure
2.65% MgO-Fine	3.5	5	5.8	8	4	Excellent	Glazed	Cracked
3% MgO	3.5	5	5.6	11	4	Excellent	Glazed	Cracked
3.05% MgO-Fine	3.5	5	6.1	4	8	Fair	No Sign	Failed, Spalli
3% CaO	3.5	5	5.7	10	8	Good	No Sign	No Failure
F410	3.5	5	5.5	13	6	Excellent	Glazed	Broken
F410	3.5	5	5.8	9	1	Excellent	Glazed	Large Open Cra
4% MgO	3.5	5	5.6	11	5	Fair	No Sign	Cracked
2.85% MgO-Med.	3.5	5	5.3	16	8	Excellent	Glazed	No Failure
3.5% CaO-Fine	3.5	5	5.9	6	4	Excellent	No Sign	Small Crack
3% Y ₂ O ₃	3.5	5	4.4	30	4	Poor	No Sign	Dinsintegrated
F410	2.0	10	5.6	20	8	Excellent	Glazed	No Failure
F410	3.5	10	5.2	26	8	Good	Glazed	No Failure
F410	5.0	10	5.1	27	8	Fair	Glazed	No Failure
F410	10.0	10	5.3	24	8	Poor	Glazed	No Failure, Spa
F410	5.0	5	5.4	15	2	Excellent	Glazed	Small Crack
F410	2.0	7	5.5	19	2	Excellent	No Sign	Cracked
2.85% MgO-Fine	2.0	10	5.9	16	5	Excellent	No Sign	Small Crack
2.85% MgO-Fine	2.0	7	5.5	19	8	Excellent	No Sign	No Failure

* Porosity is based on theoretical full density of 6.39 g/cc for 5 v/o composites and 7.07 g/cc for 10 v/o composites.

The 2.85% MgO fine-texture (Figure 24a) survived 8 cycles of the plasma jet test practically undamaged and showed the highest degree of freedom from craze cracking of any matrix material tested. The surface cracks visible in the photograph do not extend down the O.D. and do not appear to involve fiber failure. The I.D. surface has several axial cracks that do not extend the length of the specimen. No evidence of melting or tendency towards spalling were observed.

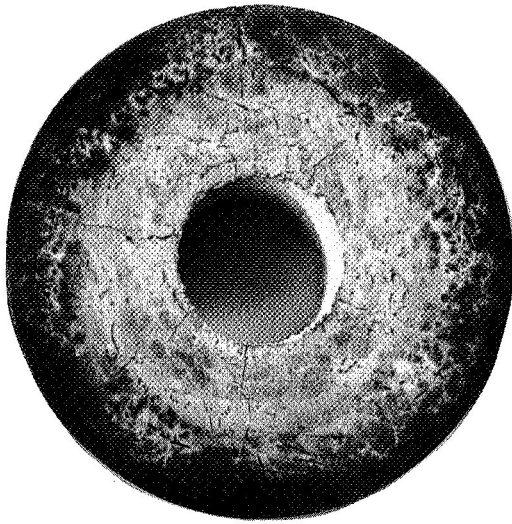
The specimen shown in Figure 24b, a 6% Y_2O_3 (95% stabilized) matrix composite, also survived 8 cycles in the plasma jet without failure. The specimen however, suffered considerable spalling of the I.D. surface. The visible cracks running from the I.D. to O.D. did not propagate axially along the cold wall. The large fissures visible in the photograph were present in the composite before testing; they resulted from the sintering cycle. This composite, while rated high in thermal shock resistance, may have questionable oxidation resistance. No evidence of melting was observed.

The 2.65% MgO matrix specimen (Figure 24c) ran 4 cycles. The test was stopped at this point because a number of cracks were opening at the specimen O.D. indicating fiber failure. No spalling and no tendency towards craze cracking were observed as a result of the test. This matrix material has good oxidation resistance potential and good fabricability with intermediate thermal shock resistance.

A 3% MgO-stabilized matrix composite is shown in Figure 24d. This test was stopped after 4 cycles because of the formation of macrocracks on the O.D. surface. The fissures visible in the photograph were present in the as-sintered specimen and did not open up during the thermal shock test. No spalling or craze cracking was observed. The I.D. of the specimen was glazed.

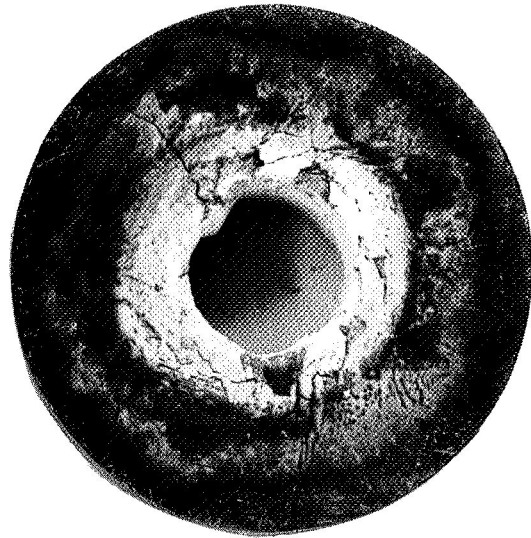
The 3.05% MgO-stabilized, fine-texture matrix composite sintered to a high density, 6.1 g/cc (4% porosity), but contained several fissures radiating from the I.D. towards the O.D. which undoubtedly lower the elastic modulus and delay thermal shock failure. This composite failed during the 8th cycle when a crack initiated at one of the fissures and propagated along the O.D. The sample suffered some spalling and had a slight tendency towards craze cracking near the hot wall surface.

The 3% CaO-stabilized composition, an off-the-shelf matrix material, survived 8 test cycles without complete failure. A number of cracks formed during the test cycles apparently involving some fiber failure but did not extend completely across the specimen. No melting was observed, but some glazing of the I.D. did occur. The specimen underwent progressive deterioration during the course of the tests but was still structurally sound.



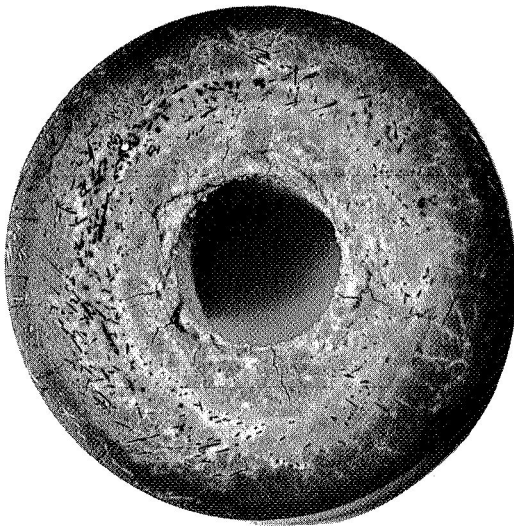
a.

2.85% MgO - fine texture matrix
5 v/o of 3.5 mil dia. wire
after 8 cycles.



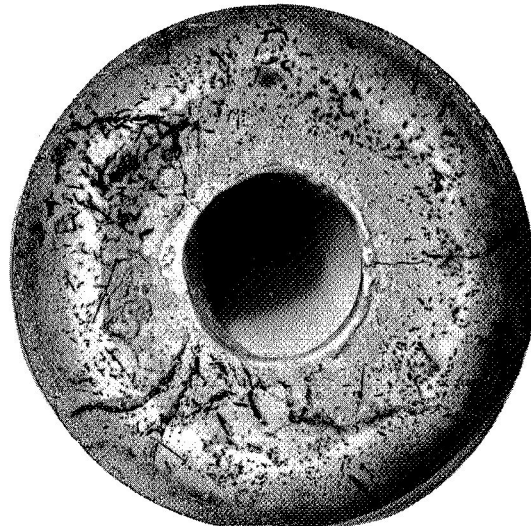
b.

6% Y_2O_3 matrix + 5 v/o
3.5 mil dia. wire
after 8 cycles.



c.

2.65% MgO fine texture
5 v/o 3.5 mil dia. wire
after 4 cycles.



d.

3% MgO matrix 5 v/o 3.5 mil
wire after 4 cycles.

Figure 24. Vacuum sintered zirconia composites reinforced with 5 v/o of 3.5 mil diameter W-3% Re wire after plasma jet thermal shock testing.

The first of two F410 matrix specimens which was 13% porous failed after the 6th cycle by the formation of two macrocracks 180 degrees apart running across the top surface and down the length of the specimen. The specimen was broken by hand flexing after the 6th cycle. No spalling or tendency towards craze cracking was evident. The I.D. surface was glazed by the plasma torch but no other signs of deterioration were present. The test was repeated with a second F410 matrix composite containing 9% porosity. The second specimen developed a macrocrack on the O.D. after a single cycle and testing was discontinued. The second specimen contained no other signs of deterioration such as spalling or craze cracking.

The 4% MgO matrix composite ran 5 cycles before the formation of macrocracks along the O.D. The cracks could be opened by manual flexing indicating fiber failure. This material also had a tendency to form straight cracks radiating out from the I.D. towards the O.D. on both ends indicating either partial failure of the fibers or failure of the fibers to stop crack propagation. Slight spalling and craze cracking also occurred. No melting of the I.D. was observed. This matrix material also has a tendency towards the formation of fissures during sintering.

The 2.85% MgO medium texture matrix material was included in the plasma jet test series because of its superior performance in the unreinforced condition in the quench test ($\Delta T = 850^\circ\text{F}$). When composited with 5 v/o of 3.5 mil diameter wire, the composite had a sintered porosity of 16%. The untested specimen had a number of small cracks as a result of poor sinterability or inferior fiber-matrix bonding. The specimen was tested for 8 cycles and showed no signs of deterioration other than minor craze cracking.

The 3.5% CaO composite was tested for 4 cycles before a macrocrack developed on the O.D. The composite showed no other signs of deterioration such as spalling, melting, or craze cracking as a result of the tests.

The 3% Y_2O_3 composite was 30% porous as sintered, very friable and subject to spalling, and contained a large number of fissures in the untested condition. Testing was stopped after 4 cycles when the specimen disintegrated.

On the basis of these tests, an overall evaluation of matrix materials was made by the combined attributes of general appearance (before and after thermal shock testing) and thermal shock behavior. By this evaluation, the promising matrix materials were narrowed to the fine-textured and medium-textured 2.85% MgO-stabilized zirconia and the F410 material.

3. Effects of Reinforcement Variables

A second series of isopressed-and-vacuum-sintered composites were tested by the plasma-jet thermal shock test in order to evaluate the effects of wire diameter and wire volume. These specimens were all fabricated with the F410 matrix material. The results of these tests are included in Table 16. The first 4 specimens in this series, all containing 10 v/o of wire reinforcement survived 8 cycles in the plasma jet with their structural integrity relatively undamaged. The specimen shown in Figure 25a reinforced with 10 v/o of 2-mil diameter wire, was virtually unchanged in appearance as a result of the 8 test cycles except for the I.D. surface where some of the reinforcement wires were lost. The 3.5 and 5-mil diameter wire composites, Figure 25b and 25c, are also relatively undamaged except for slight spalling at the I.D. edges. The 10-mil wire diameter composite (Figure 25d) suffered considerable spalling particularly at the O.D. edges but was otherwise unaffected by the thermal shock test cycles.

It is seen, therefore, that the tendency for spalling increased as the wire diameter increased from 2 mils to 10 mils. The formation of fissures during sintering was also the most pronounced in the 10-mil wire diameter composite and negligible in the smaller wire sizes. These fissures, however, did not serve as crack propagation sources in any of the 10 v/o composites. All 10 v/o reinforced composites demonstrated excellent thermal shock crack resistance and a high degree of resistance to general degradation from the thermal shock cycles.

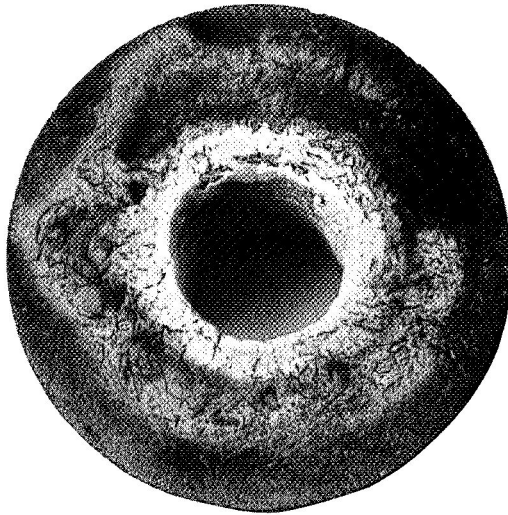
The fifth specimen in this series was an F410 matrix, 5 v/o 5-mil diameter wire composite. The testing of this composite was discontinued after 2 cycles because of a macrocrack formed on the O.D. of the specimen. The specimen showed no other signs of deterioration such as spalling or craze cracking as a result of the 2 test cycles.

These data show that the 10 v/o wire composites offer better thermal shock resistance than the 5 v/o composites, but that the general integrity and visual appearance is degraded by the greater wire content - particularly with the thicker wires. This behavior suggests then, that composites with an optimum compromise of properties might be obtained by the use of intermediate wire contents of the smaller diameter wires.

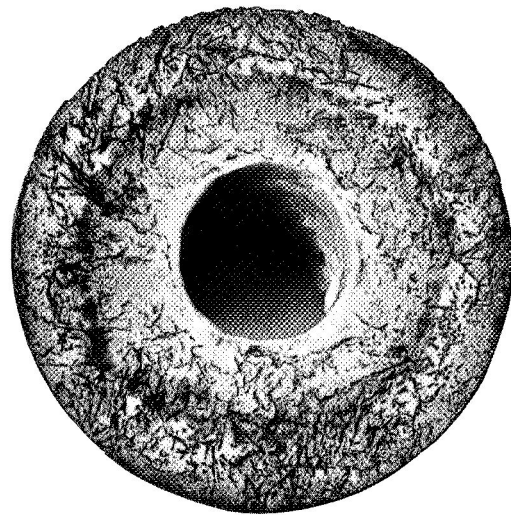
4. Testing of Optimized Composites

Based on the results of the two previous series of tests, an effort was made to combine the best matrix materials with the optimum combination of reinforcement variables.

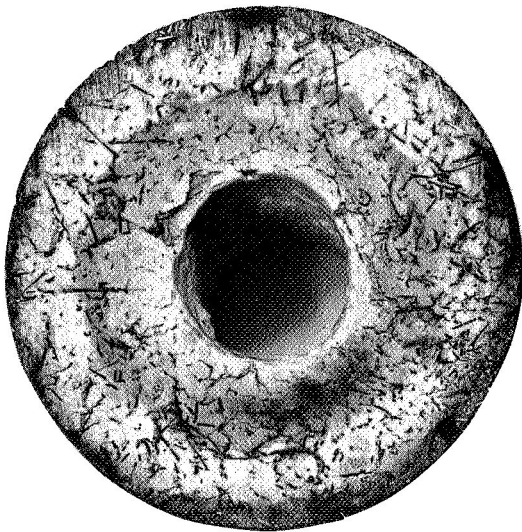
Three additional composite materials were fabricated by vacuum sintering for these additional tests. These specimens consisted of the 2.85% MgO-stabilized fine-texture matrix material reinforced with 7 and 10 v/o of 2-mil diameter wire and an F4.0 matrix - 7 v/o 2-mil wire composite.



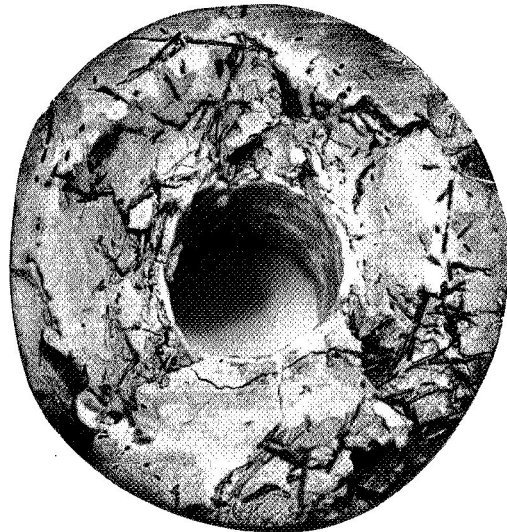
a. - 2.0 mil wire dia.



b. - 3.5 mil wire dia.



c. - 5.0 mil wire dia.



d. - 10.0 mil wire dia.

Figure 25. Isopressed and vacuum-sintered composites reinforced with 10 v/o of W-3% Re wire after 8 cycles in the plasma jet thermal shock test.

The results of plasma-jet thermal shock tests of these materials are included with the previous data in Table 16.

The 2.85% MgO-stabilized zirconia composite reinforced with 7 v/o of 2-mil diameter wire contained a few small fissures or areas of high fiber concentration in the as-sintered condition. There was no tendency towards craze cracking or spalling. The specimen survived 8 cycles in the plasma-jet thermal shock test with no visible damage except for the I.D. where reinforcing fibers were lost to a depth of approximately 50 mils. The O.D. contained no visible cracks, no craze cracking, and no spalling. The I.D., which showed no signs of melting or glazing, had 2 cracks 180 degrees apart running the full length of the specimen and apparently 50 mils deep. The visual appearance of this composite was rated excellent.

The specimen fabricated with the same matrix material and reinforced with 10 v/o of 2-mil diameter wire contained more fissures than the 7 v/o wire composite and exhibited a slight tendency towards craze cracking in the as-sintered condition. After 4 cycles in the plasma-jet thermal shock test, a crack initiated at one of the fissures on the O.D. Because the crack had not propagated completely across the top or bottom, the specimen was recycled. Since there were no observable effects from the 5th cycle and the crack had not propagated any further, testing was stopped at this point. There was no additional craze cracking, no spalling, and no indications of melting of the I.D.

The as-sintered F410 matrix 7 v/o of 2-mil wire composite contained a number of fissures and high fiber concentration areas, comparable to the 2.85% MgO 7 v/o wire composite. The specimen also included some craze cracking on the O.D. surface. After 2 cycles in the thermal shock test, an open crack developed on the O.D. and propagated across the top and bottom and down the length of the I.D. The specimen also developed a number of additional craze cracks on the O.D. The I.D. surface was glazed. No spalling was noted on this specimen.

From these tests, the best composite appears to be the 2.85% MgO-stabilized matrix containing 7 v/o of 2-mil diameter wire. The 7 v/o of 2-mil wire in the F410 matrix does not seem to be any better a reinforcement system than 5 v/o of the 3.5 mil wire which was tested previously.

5. Hot-Pressed Specimens

A series of composites reinforced with 5 v/o of 3.5 mil diameter tungsten wire were fabricated by hot pressing for evaluation in the plasma jet thermal shock tests. The matrix materials were blends of monoclinic zirconia with Ti, Y_2O_3 and CeO_2 stabilizers and were fabricated by means of reactive hot pressing cycles. An additional series of composites using the F410 matrix material, a prestabilized composition, were hot pressed using more conventional pressing cycles for inclusion in the plasma jet thermal shock test program.

The results of plasma jet thermal shock testing of hot-pressed composites are presented in Table 17. The appearance of the specimens is presented in Figure 26. A brief description of composite behavior during testing is detailed below.

The 6% Ti-stabilized zirconia composition had the highest ΔT (1275°F) of any unreinforced matrix material tested in the thermal shock quench test. The hot pressed composite reinforced with 5 v/o of 3.5 mil wire failed in a single cycle in the plasma jet test through formation of a large macrocrack on the cold wall. The specimen also underwent considerable melting of the matrix material to a depth of approximately 0.100 inch along the entire length of the I.D. The melting apparently left the reinforcing wires intact.

The reaction of both CeO₂-stabilized composites was similar. Both specimens failed in a single test cycle by macrocrack formation along the length of the O.D. Melting of the I.D. also occurred on both specimens with the 10% CeO₂- stabilized composition exhibiting more pronounced melting. Neither composite showed craze cracks or other signs of progressive deterioration.

The 3% Y₂O₃-stabilized composite failed in a single cycle and also suffered delamination as the result of the test. The porosity of this specimen was 16%. A 5% Y₂O₃-stabilized composite of 20% porosity was also included in the test program and failed in a single thermal shock cycle.

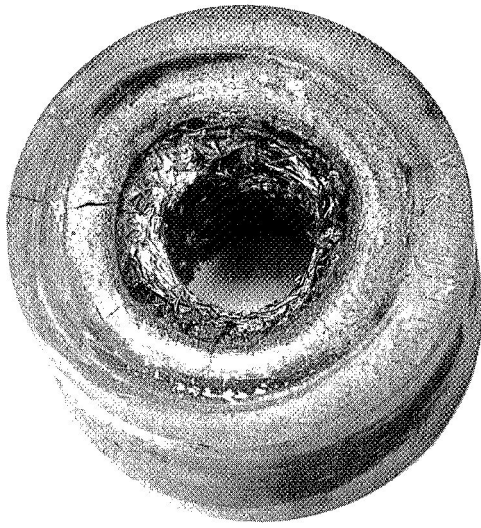
A series of F410 matrix composites containing various degrees of porosity were also tested to determine the effects of porosity on hot-pressed compacts and also to provide a direct comparison between hot-pressed and vacuum-sintered composites of comparable porosity. These composites were all reinforced with 5 v/o of 3.5 mil wire. Specimens containing 1, 2 and 10% porosity were tested. All three of these hot pressed F410 zirconia composites failed in one test cycle through formation of relatively large, open macrocracks. An examination of the fracture surface revealed no evidence of fiber pullout and indicated that tensile failure of the reinforcement had occurred. No other signs of deterioration were observed.

A hot-pressed composite of Zyttrite matrix reinforced with 5 v/o of 3.5 mil wire was included in the test. Zyttrite is a 10% Y₂O₃ fully-stabilized zirconia composition prepared by decomposition of the alkoxide resulting in an ultra-high-purity, ultra-fine-particle zirconia. The composite was pressed at 2800°F for 10 minutes at 8000 psi and was 16% porous as tested. The specimen survived 8 cycles in the plasma jet test without failure. The specimen had, however, suffered severely from craze cracking. This craze cracking and resulting lack of good visual appearance prevented this material from being considered for further inclusion in the program. The price of Zyttrite, which is currently over \$500/lb, is an additional reason for not pursuing this material further.

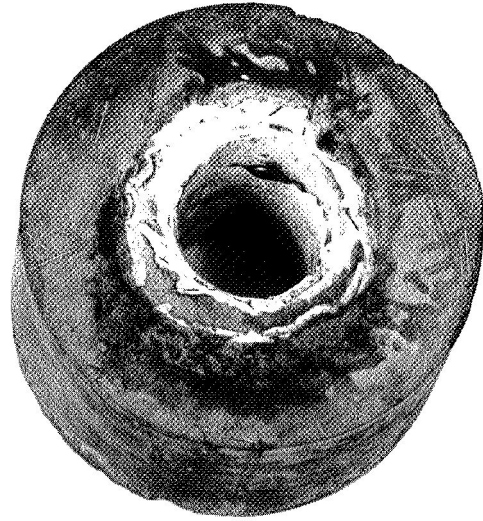
TABLE 17

PLASMA JET THERMAL SHOCK TEST RESULTS OF HOT-PRESSED ZIRCONIA COMPOSITES
 REINFORCED WITH 5 v/o OF 3.5 MIL DIA x 3/16" LONG W-3%Re WIRE

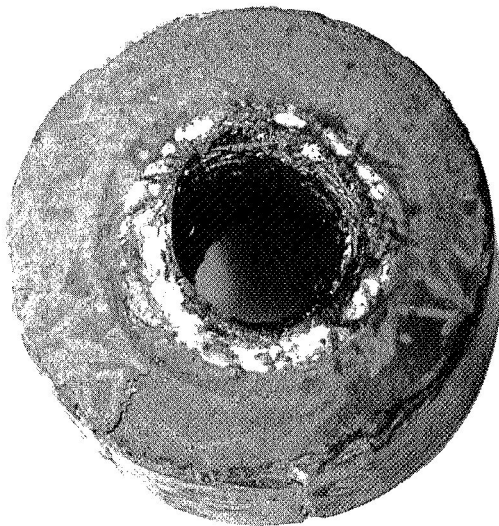
Matrix Material	Hot Pressing Cycles	Density g/cc	Porosity %	Thermal Shock Test Cycles	Visual Appraisal	Melting	Comments
6% Ti	10 @ 2500°F	5.8	8	1	Excellent	Excessive	Excessive melt.; cracked
5% CeO ₂	15 @ 2500°F	5.8	8	1	Excellent	Slight	Slight melt., crack
10% CeO ₂	15 @ 2500°F	6.0	5	1	Excellent	Moderate	Melt., Cracked
3% Y ₂ O ₃	2 cycles @ 1900°F-2300°F	5.3	16	1	Poor	Glazed	Cracked; Delaminated
5% Y ₂ O ₃	15 @ 2300°F	5.1	20	1	Excellent	None	Cracked
F410	10 @ 2800°F	6.3	1	1	Excellent	Glazed	Broken
F410	10 @ 2600°F	6.2	2	1	Excellent	Glazed	Broken
F410	10 @ 2600°F	5.6	10	1	Excellent	Glazed	Open Cracks
Zyttrite	10 @ 2800°F	5.3	16	8	Fair	None	Craze Cracking



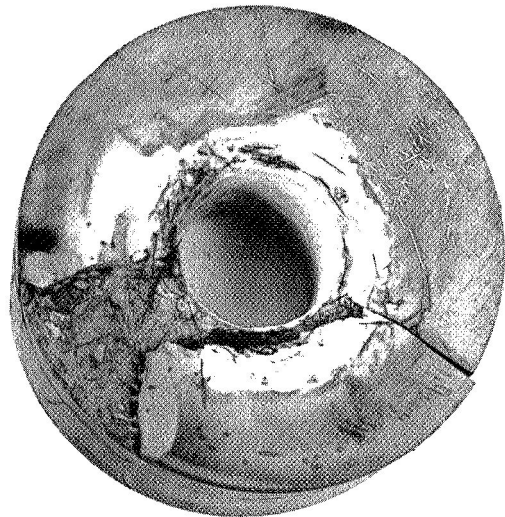
a. 6% Ti Matrix



b. 5% CeO₂ Matrix



c. 10% CeO₂ Matrix



d. 3% Y₂O₃ Matrix

Figure 26. Hot-pressed zirconia composites reinforced with 5 v/o of 3.5 mil diameter W-3% Re wire after a single cycle plasma jet thermal shock test.

All of these hot-pressed composites exhibited some shortcoming, so hot pressing was eliminated from further consideration in this program. based on these thermal shock tests.

6. Selection of Composites for Remainder of Program

Based on these plasma-jet thermal shock tests, sufficient information was available to permit a choice of composite materials for further evaluation in the remainder of the program. Based on the thermal shock results summarized in Table 16 combined with data from Task 1 of the program, the following three materials were chosen for further study:

<u>Identity Code</u> <u>Designation</u>	<u>Zirconia</u> <u>Matrix Type</u>	<u>Reinforcement</u> <u>(W-3%Re Wire)</u>	<u>Reasons for Choice</u>
Type A	F410	5 v/o 3.5 mil x 3/16" long	Good Thermal shock Best overall visual appearance. Good base for comparison of other data
Type B	2.85 MgO stabilized Medium Texture	5 v/o 3.5 mil x 3/16" long	Excellent thermal shock Excellent overall visual appearance
Type C	2.85 MgO stabilized Fine Texture	7 v/o 2.0 mil x 1/8" long	Excellent thermal shock Excellent overall visual appearance

Specimens of these three composite material compositions, fabricated in each case by the isopress-and-vacuum-sinter approach, were evaluated in subsequent parts of the program. This evaluation included further thermal shock tests by an electron beam heated apparatus, thermal and mechanical property tests in Task 3 of the program, and oxidation tests in Task 4. This battery of tests then allowed the selection of the best of these materials for fabrication, in Task 5, of a throat insert for testing.

C. Electron Beam Tests

For the composite material to be used for final throat insert fabrication in this program, it was desired to perform a more complete study of its thermal shock behavior. For these tests, a thermal stress test apparatus at TRW Systems, Redondo Beach, California was used. This apparatus, which uses an electron beam heating source, provided a more quantitative evaluation of thermal shock behavior because of the ability to measure directly the heat flux to the specimen and also monitor temperature and strains experienced by the specimen.

Because of the time and cost involved in these tests, it was decided to apply this technique primarily to the two most promising composites. By the time these tests were to be implemented, results from Tasks 3 and 4 (particularly the rocket exhaust oxidation tests in Task 4) indicated that the Type C and the Type A materials (in that order), as designated above, showed the best composite properties. Therefore, the thermal shock test effort was concentrated on these two composites with the appropriate priority given to each. Type B specimens were also prepared but were used mainly for trial runs of the apparatus.

1. Test Description

The electron beam heating system used as the heat source is rated at 75KW and can deliver heat fluxes in excess of 10,000 BTU/ft²-second. It can be automatically controlled to give constant heat fluxes or a particular thermal transient. The test employs a cylindrical type specimen 1" I.D. x 1-1/2" O.D. x 1/2" high. A schematic view of the specimen and electron gun are shown in Figure 27.

Because direct electron beam heating requires that the specimen be an electrical conductor, duplicate specimens of each of the 3 composite materials were molybdenum coated on the I.D. surface by vapor deposition. A tungsten coating was applied to the ends of the specimen by plasma spraying for additional conductivity.

2. Testing and Results

The thermal shock analysis of the composite materials was performed by TRW Systems. Preliminary testing of the Type B specimens indicated that this material was the least promising of the three materials being tested and a complete analysis of the Type B material was not performed. The testing and results of the Type A and C material were as follows:

Type C material - Two thermocouples were spot welded to the top surface of the sample at 33 and at 235 mils from the inside surface. The sample was baked out at 1850°F for one hour and cooled to room temperature in helium. The chamber was opened and the extensometer was installed. The sample was again baked out at 1850°F for 5 minutes and let cool to room temperature in a vacuum.

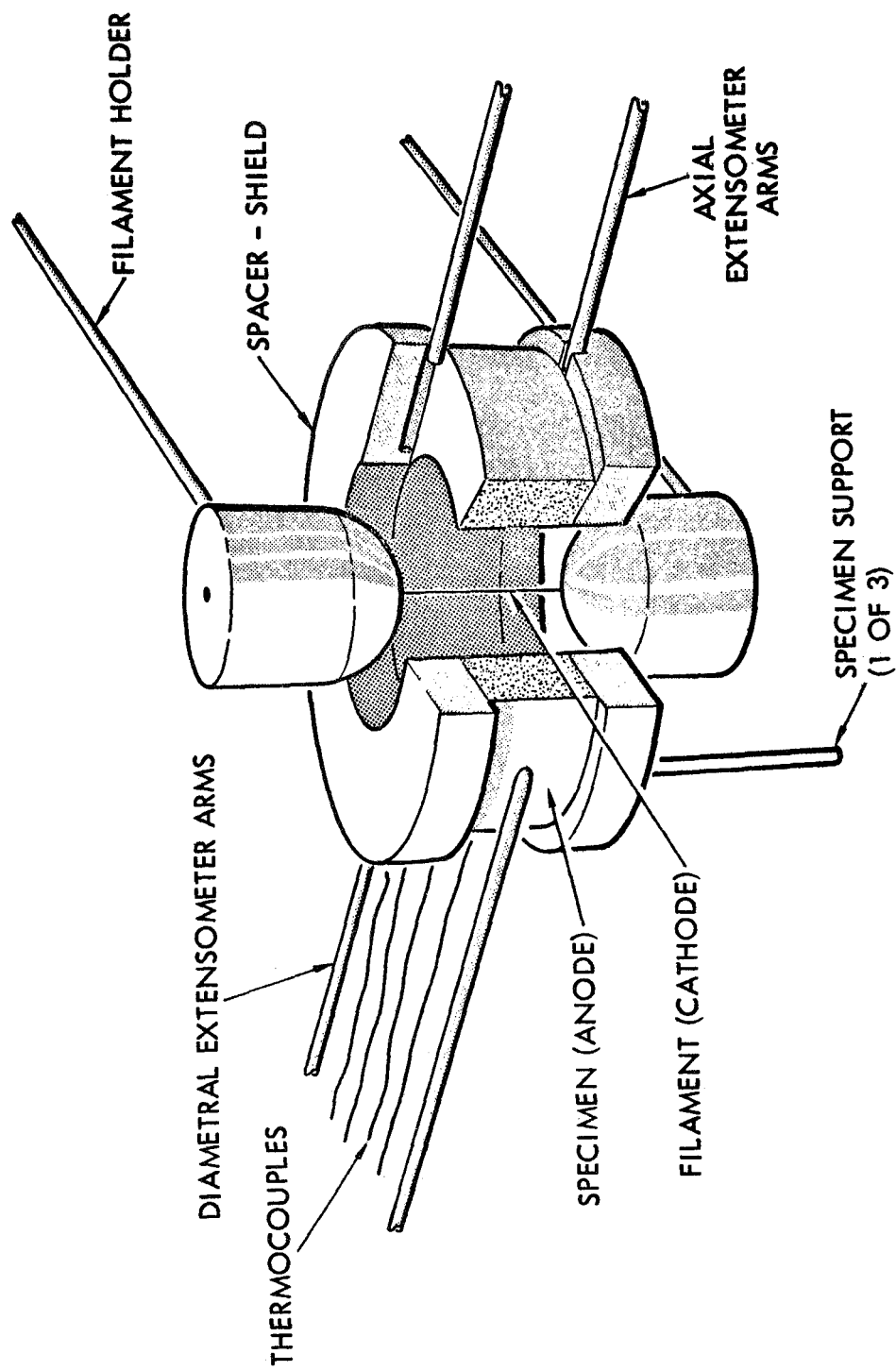


Figure 27. Cutaway view of thermal shock specimen and associated electron gun components of electron beam thermal shock test apparatus.

Run 1 - The power supply was set for a maximum output power of 60KW. The sample received a peak power of 20KW which caused melting of the inside surface of the sample and produced arcing. The sample was run for about three seconds under this condition. The maximum temperature reached at the inside thermocouple at three seconds was 2000°F. The outside thermocouple at three seconds reached at temperature of 500°F. The outside diameter of the sample increased about 8 mils at 3 seconds. The sample was then allowed to cool to room temperature.

Run 2 - The power supply was set for a maximum output power of 28KW. The sample received a peak power of 4KW which reduced the violent melting of the inside surface of the sample. This test was run for 32 seconds. The inside thermocouple reached a temperature of 2850°F; the outside thermocouple 1850°F. The maximum change in diameter increased to 14.5 mils at 32 seconds.

Run 3 - With the same power supply setting as Run 2, the peak power to the sample was 6 KW. The total run time was 20 seconds. The maximum inside thermocouple temperature was 2550°F; the outside thermocouple temperature reached 1250°F. The maximum increase in diameter was 14 mils.

A second sample of this material was instrumented with three thermocouples located at 80, 117, and 195 mils from the inside surface of the specimen. With a power supply setting of 28KW, the sample received a peak power input of 5KW. The resultant temperature gradients and sample dimensional changes for a 40-second duration test under these conditions are shown in Figure 28. The appearance of this specimen after testing is shown in Figure 29a. It is evident that some melting of the inside surface took place indicating that a temperature in excess of 4700°F at this surface was attained during the test.

Type A materials - Samples of this material were run using the same 3-thermocouple instrumentation and instrument power settings as the second sample of the Type C material. The power to the sample and the resultant temperatures and dimensional changes in the specimen during an 18-second duration run are plotted as a function of time in Figure 30. An additional run with this specimen was carried out for 40 seconds during which the power input of 8KW was delivered to the specimen. The specimen after testing is shown in Figure 29b. Again, the inside surface of the specimen shows evidence of surface melting, thereby indicating the attainment of surface temperatures in the 4700°F range.

3. Interpretation of Test Results

All of the composite specimens tested in the electron beam thermal shock tests survived the thermal environments imposed by a 4 to 8 kilowatt heat input to the specimen. Some of these specimens were tested for times up to 40 seconds. In no case did a specimen fail by complete fracture.

The power input can be converted approximately to BTU/ft²-sec heat flux units by multiplying the power in kilowatts by 80.

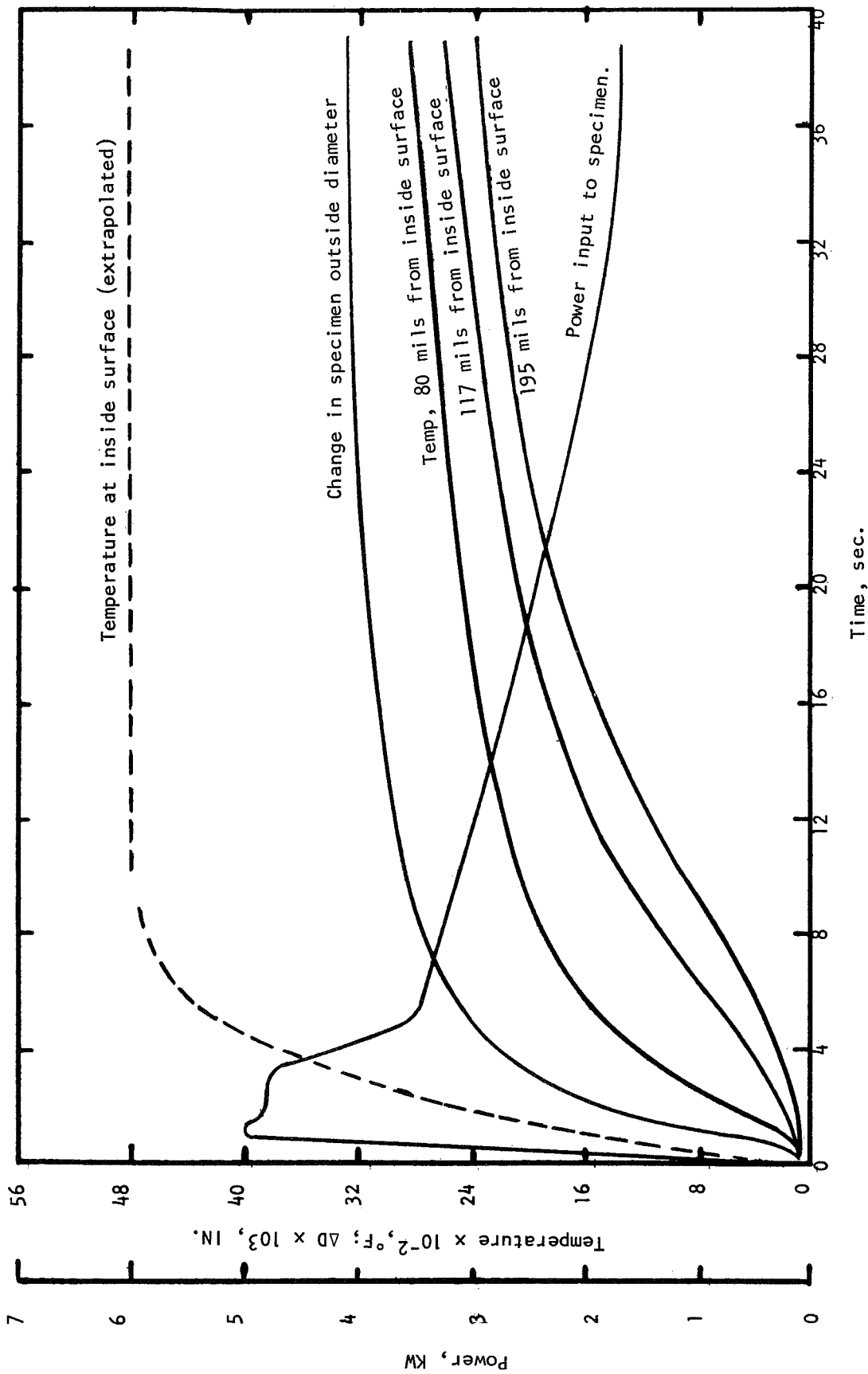
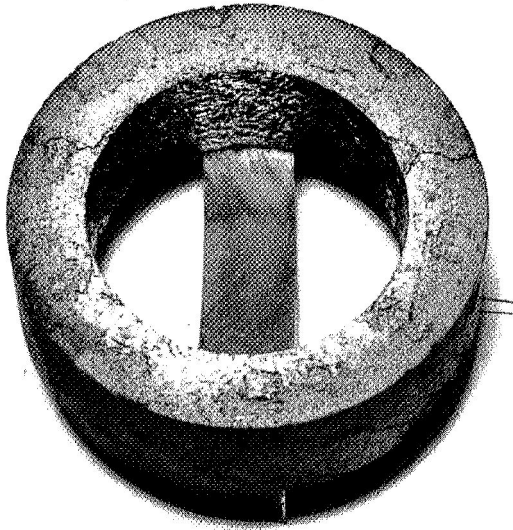
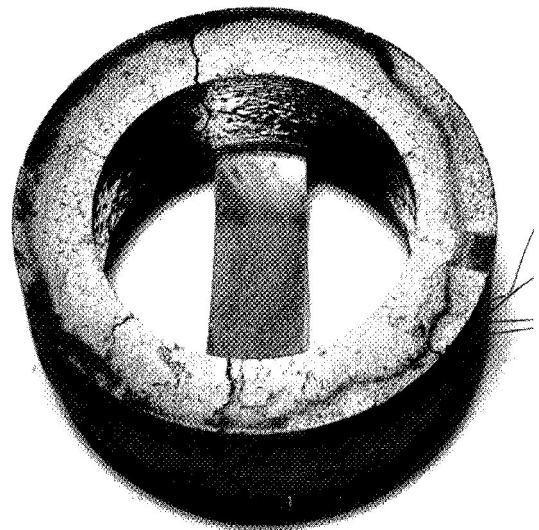


Figure 28. Power input to sample, temperature, and dimensional change of a Type C reinforced zirconia composite during electron beam thermal shock tests.



a. Type C Material Specimen
2.85 MgO Zirconia Matrix
+ 7v/o of 2.0 mil W-3%Re
Wire.



b. Type A Material Specimen
F410 Matrix + 5v/o of 3.5
mil W-3%Re Wire.

Figure 29. Electron beam thermal shock specimens after testing.

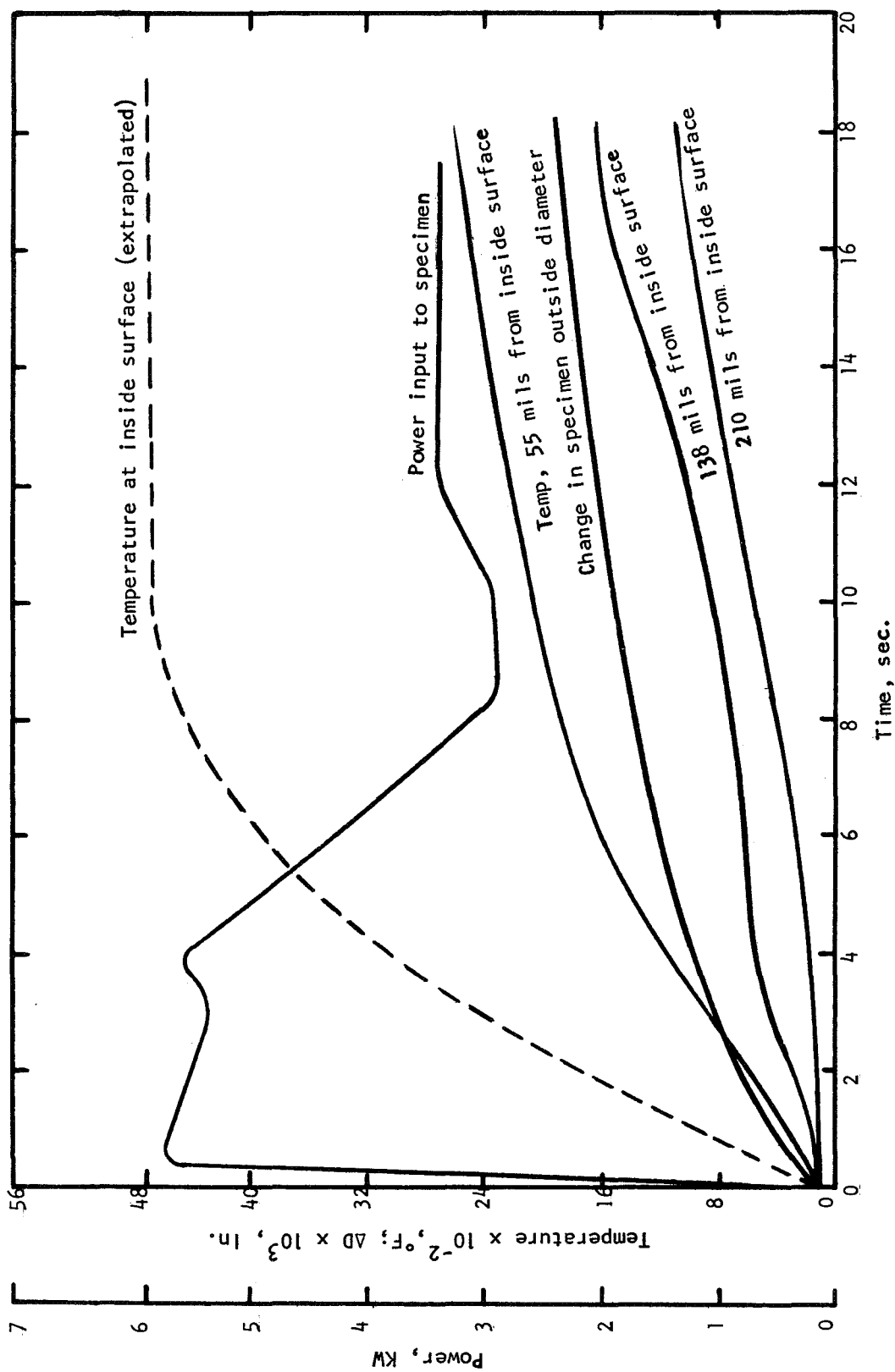


Figure 30. Power input to specimen, temperature and dimensional change of Type A reinforced zirconia composite during electron beam thermal shock tests.

Therefore, some specimens, which reached a peak power input of 8 KW, incurred a heat flux of about 640 BTU/ft²-sec. As noted above, however, this heat flux caused severe melting on the inside surface of the specimen. A heat input to the specimen of about 5KW (400 BTU/ft²-sec) was the maximum that could be maintained for more than a few seconds. These lower-power, sustained tests probably resulted in less melting and, therefore, probably greater transfer of hoop stress to the O.D. of the specimen. In this regard, they were probably the most severe tests from a thermal stress cracking standpoint.

The appearance of the specimens after these tests, as illustrated in Figure 28, indicate that the Type C composite, which is reinforced with 7 v/o of 2-mil diameter wires, has less tendency to form large, open cracks than the Type A composite, which contains 5 v/o of 3.5 mil wire. The Type C material, therefore, would be expected to perform better than the Type A material in a nozzle subjected to multiple firing cycles because of the better protection of the reinforcing fibers from oxidation.

In addition to this qualitative interpretation of the data, it was desirable to make a more quantitative analysis of the thermal shock behavior of these composites. The electron beam test has been normally used to rate materials by measuring the heat flux that will cause failure of the specimen. An alternate rating used has been the time to failure at a fixed heat flux. Since none of these zirconia specimens could be broken by the maximum applicable heat flux, neither of these rating criteria can be used in a quantitative manner. These reinforced zirconia composite form a microcracked matrix which is held together by the reinforcing fibers. This stress relief mechanism allows a type of ductile behavior in the composite and prevents complete fracture of the specimens.

The best evaluation of these composites can therefore, be made by comparing their behavior during this test with that of other types of candidate rocket nozzle materials that have been subjected to this test. A series of carbide-graphite materials had been tested in this apparatus and were rated on the basis of the power input versus time to failure. The data from these carbide material are plotted in Figure 31. The dashed line in this plot represents a combined power-time condition beyond which (i.e. either increased power or time) the composite carbides fail in thermal shock. Included for comparison in this plot are points representing the test parameters of the various tests of the zirconia composites. It is significant to note that the severity of test conditions of the zirconia composites far exceeded those of the carbide composites, and that none of these zirconia composites were completely fractured by these tests.

In summary, the electron beam tests have demonstrated that the zirconia composite materials are not subject to catastrophic failure from severe thermal shock environments. This of course, is in agreement with the plasma jet thermal shock tests performed earlier in the program.

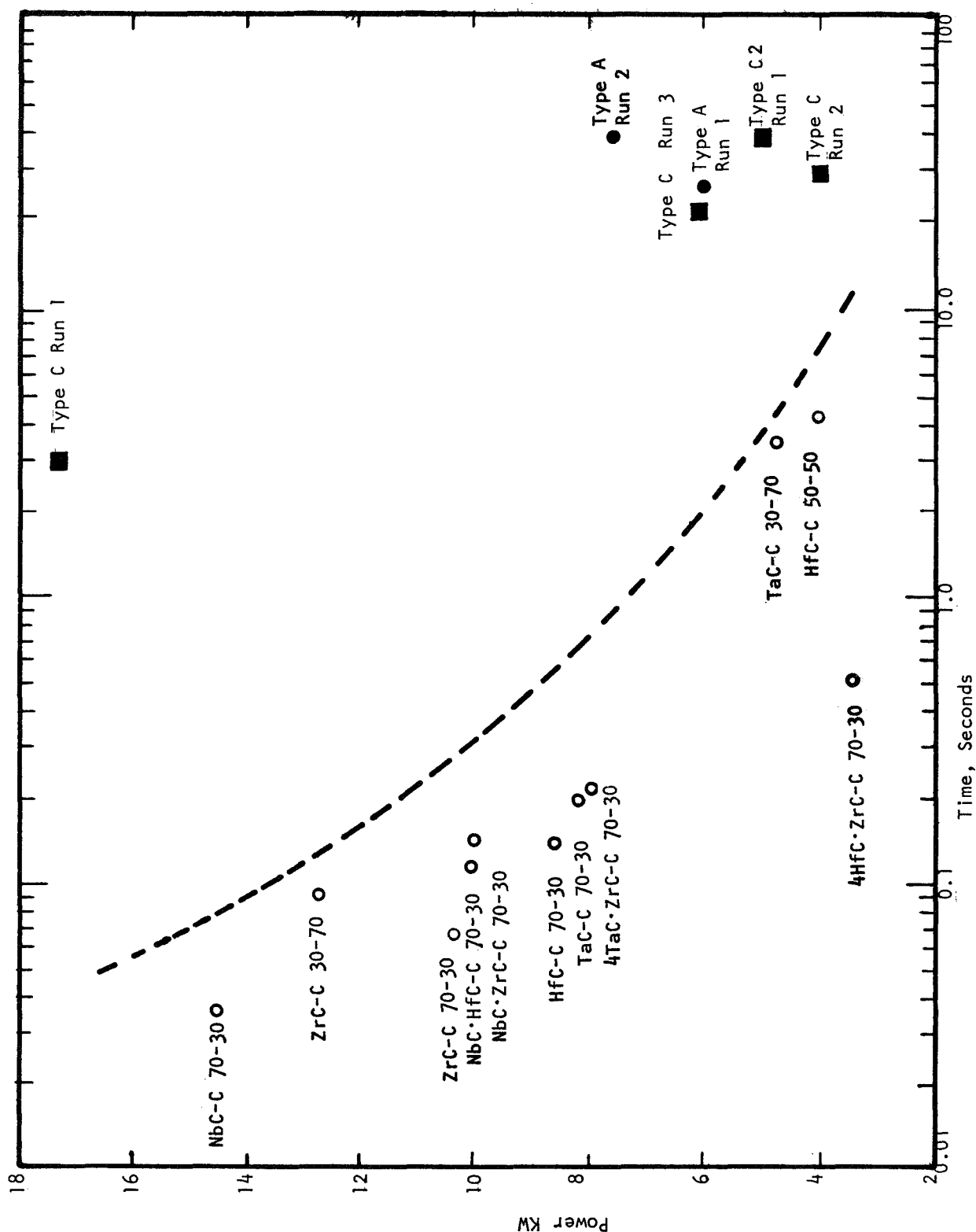


Figure 31. Thermal shock behavior of candidate throat insert materials in the electron beam test. Dashed line represents a condition beyond which (i.e. either increased power or time) composite carbides fail in thermal shock. The reinforced zirconia far exceeded the severity of these conditions without complete failure in any case.

This test also indicated that the Type C composite (the 2.85% MgO stabilized zirconia reinforced with 7 v/o of 2-mil wire) may be the best composite for use in subsequent fabrication of throat inserts for test firing evaluation.

A comment is in order concerning the applicability of the electron beam thermal shock test for this type of composite material. In general, the technique seems to be a good one when, as in these tests, the specimens are given a conductive coating to aid in the electron current flow. The ability to quantitatively measure the actual heat flux into the specimen is an advantage. However, because of the limited scope of tests performed on this program, these advantages could not be fully exploited. The information of meaning to this program was mainly that of confirming a choice of material already evident by prior tests.

TASK 3- THERMAL AND MECHANICAL PROPERTIES

The aim of this part of the program was to determine those thermal and mechanical properties of the reinforced oxide composites pertinent to the design and analysis of nozzle configurations. The first property of interest was the bond strength between the matrix and reinforcing fiber; this would determine the optimum fiber aspect ratio for use in the composite development phase of the program. Subsequent work in this task consisted of measuring the pertinent properties of the three materials (Type A, Type B, and Type C*) identified as the most promising at this point in the program. The properties tested included: tensile strength, compressive strength, elastic modulus, thermal conductivity, and thermal expansion. In each case, the properties were determined as a function of temperature insofar as available experimental techniques allowed. This information was then useful in the selection of the material for test-nozzle fabrication and in the design analysis of the nozzles.

A. Fiber-Matrix Bond Test

It was desired to know the interface bond strength between the matrix and the reinforcing fiber. This property is an important factor in determining the optimum reinforcement aspect ratio. This bond strength value multiplied by the surface area of the fiber should be at least equal to the tensile strength of the fiber. If it is not, the full strength of the fiber can never be utilized because the interface bond will limit the transfer of stress to the fiber. The length of fiber which provides sufficient surface area for these strengths to be equal is termed the critical length. If the fiber length is many times longer than this critical length, the composite will probably not be as efficient as it would be if a greater number of shorter fibers were more homogeneously distributed throughout the matrix. By determining this bond strength, a guideline for the desired length of any diameter reinforcing wire can be obtained.

It was planned to determine this bond strength value by a fiber pull-out test. When this approach proved inappropriate because of experimental difficulties, a more empirical approach to fiber aspect ratio was employed by measuring bend strengths of samples prepared with controlled variations of fiber aspect ratio.

* The composition of these composites are as follows:

Type A An F410 matrix reinforced with 5 v/o of 3.5 mil diameter x 3/16 inch long W-3%Re wire.

Type B A 2.85% MgO-stabilized medium-texture matrix reinforced with 5 v/o of 3.5 mil diameter x 3/16 inch long W-3%Re wire.

Type C A 2.85% MgO-stabilized fine-texture matrix reinforced with 7 v/o of 2-mil diameter x 1/8 inch long W-3%Re wire.

1. Fiber Pull-Out Testing Approach

This test typically involves the use of a button-head of matrix material with a fiber of the reinforcement embedded to a known depth. The force needed to extract the wire from the matrix material (determined by a tensile test) divided by the interface area defines the bond strength. If the fiber should fail in tension rather than be extracted from the matrix, then alternate specimens must be prepared with less interface area.

For this program, a button head of F410 zirconia was used with W-3%Re wires embedded into it. A vacuum-sintering cycle of 4000°F for 4 hours was used to sinter the zirconia and effect the fiber matrix bond. Wire embrittlement occurred during this sintering cycle to such a degree that the resulting specimens were not suitable for tensile testing. The wires of these test specimens were embrittled during sintering to a greater degree than similar wires treated by the same temperature cycle without the presence of zirconia. Apparently at the vacuum sintering temperature, a slight partial pressure of oxygen is generated by the zirconia which results in wire embrittlement. As a result, no quantitative measurement of interface bond strength could be obtained for these composites by this technique.

2. Bend Tests

Because of the problems encountered in fabricating button-head specimens for a fiber pull-out test, it was decided to determine optimum reinforcing wire aspect ratios by a more empirical type of test. This test consisted of bend testing composite specimens containing the same volume fraction of reinforcement wires of various aspect ratios. A range of wire diameters was included in this test. It was also considered that the most realistic evaluation of fiber-matrix bond strength would be to test composites after they were subjected to a thermal shock treatment to form a microcracked matrix. This would require that the fibers carry the bulk of the load through the matrix-fiber interface load transfer mechanism. Specimens were tested, therefore, in both the as-sintered and in the thermal-shocked condition.

An F410 matrix material reinforced with 5 v/o of W-3% Re wire was used for these tests. The various wire diameter and aspect ratios included in this study were as follows:

Wire Aspect Ratio	Fiber Diameter			
	<u>2.0 mil</u>	<u>3.5 mil</u>	<u>5.0 mil</u>	<u>10.0 mil</u>
63	x		x	x
54		x		
37		x	x	x
25		x	x	
12				x

The specimens for these tests were fabricated by the standard isopressing and vacuum-sintering treatment (30,000 psi pressing pressure, and a 4000°F 4 hour sintering cycle). The thermal shock treatment used consisted of a single quench from 1930°F into an ice brine solution; this was adequately severe to accomplish the purpose of this treatment. The specimens were then machined and tested by a 3-point bend test.

The bend test results of both the as-sintered and the thermally shocked composite materials are shown in Table 18. Bend strength of the thermally shocked composites are plotted as a function of aspect ratio in Figure 32. These data show that the higher values of fiber aspect ratio resulted generally in the higher strength composites and in the best strength retention in the thermally shocked samples. In fact, these data might indicate the desirability of even higher fiber aspect ratios. However, longer fiber lengths cannot be uniformly distributed throughout the matrix material by present handling and mixing techniques.

The tendency of chopped wires to mat or form fiber balls increases as the aspect ratio increases. Wires with an aspect ratio of 37 or less act in many ways as a powder material and may be mixed and handled by the same techniques used in handling coarse powders. Fibers with aspect ratios of about 60 become borderline in this respect and require careful blending and mixing to insure against the presence of fiber balls. Zirconia powder blends with such fibers are not free flowing, and must therefore be loaded into molds with utmost care to insure homogeneous distribution and random orientation of the fibers. These problems become unmanageable when wire aspect ratios much greater than 60 are used unless completely different handling techniques would be developed.

On the basis of these factors, an aspect ratio in the range of 60 appeared to offer the optimum conditions of strength retention and ease of fabrication; therefore, fiber aspect ratios in this range were used during the balance of this program. Actually, in order to work with lengths of convenient units, the 3.5 mil diameter wire was purchased to a 3/16-inch length for an aspect ratio of 54; the 1/8" long 2-mil wire and proportionate lengths of the 5, 10, and 20-mil wire had an actual aspect ratio of 63.

B. Tensile Tests

Tensile tests were conducted on the Type A, Type B and Type C composite materials developed in this program.

These tests were conducted on an Instron test stand using a cylindrical specimen of the geometry shown in Figure 33. The test stand was equipped with a resistance heated vacuum furnace capable of operating at 4000°F with a vacuum pressure of 10^{-5} torr or less. Temperatures were measured with an optical pyrometer. A cross-head speed of 0.020 inches per minute was used for all tests.

TABLE 18

FIBER MATRIX BOND TEST

Isopressed and Vacuum-Sintered Composites of F410 Zirconia Matrix
Reinforced with 5v/o of W-3%Re Wire

Wire Diameter, mils	Wire Length, mils	Aspect Ratio	Density g/cc	Porosity %	Bend Strength As-Sintered, KSI	Bend Strength After Thermal Shock, KSI
2.0	125	63	5.8	8	14.2	0.2
3.5	187	54	5.8	8	17.3	10.2
3.5	125	36	5.7	9	12.1	4.4
5.0	312	63	5.7	9	16.6	7.0
5.0	187	37	5.5	13	12.8	3.8
5.0	125	25	5.9	7	11.4	4.7
10.0	625	63	5.7	10	4.7	5.6
10.0	375	37	6.0	6	13.5	4.2
10.0	125	12	5.6	12	6.1	3.8

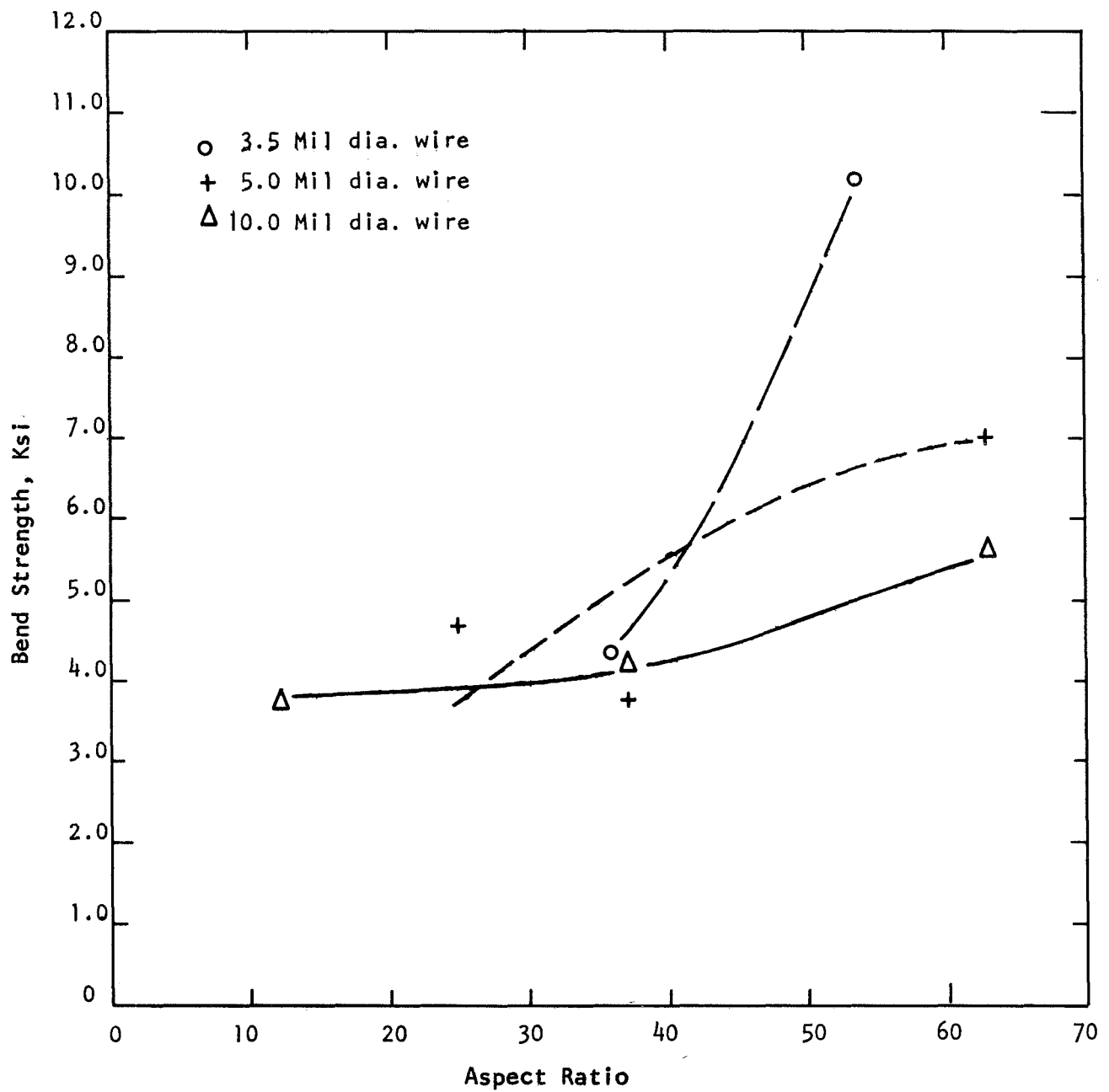


Figure 32. Bend strength of reinforced zirconia composites as a function of reinforcement aspect ratio. Specimens are vacuum-sintered composites of F410 zirconia reinforced with 5v/o W-3%Re wire after thermal shock treatment by a quench from 1930°F.

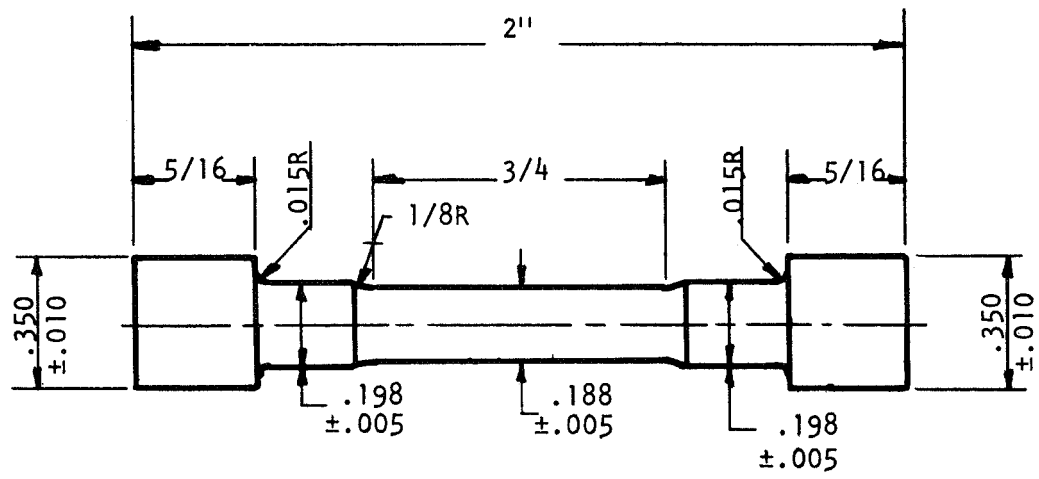


Figure 33. Tensile Specimen used for Reinforced Zirconia Material

Ultimate tensile strengths of the 3 composite materials are tabulated as follows:

Material	Ultimate Tensile Strength - psi			
	R.T.	2000°F	3000°F	4000°F
Type A	580	770	-	-
Type B	-	-	-	-
Type C	2030	2260	510	-

Type A specimens tested at 3000 and 4000°F and all of the Type B specimens fractured at loads too small to allow a valid measurement to be obtained. The Type C material at 4000°F also fractured at an unmeasurably small load. The 2000°F strengths were higher than the room-temperature strengths for both the Type A and Type C material. This behavior is probably due to the decreased brittleness of the zirconia normally associated with higher temperatures which would decrease the chance for premature brittle failure of the specimen.

A typical load-deflection curve of the Type C material is presented in Figure 34. The curve indicates brittle failure of the matrix with a subsequent transfer of the load to the more ductile reinforcing wires which prevent complete failure of the composite material. A modulus of elasticity of 0.37×10^6 psi was derived from the load-deflection curves of the Type C material. The low modulus is attributed to the presence of microcracks which may be sufficiently large in relation to the small specimen cross-section to account for this behavior.

C. Compressive Strength Tests

Compressive strength measurements of the 3 composite materials were carried out on an Instron test stand using a cross-head speed of 0.02 inches per minute. The specimen geometry was a 0.250 inch diameter x 0.500 inch long cylinder. Tests were conducted at room temperature and at a nominal 2200°F temperature in an argon atmosphere. The test fixture is shown schematically in Figure 35.

Compressive strength data are tabulated in Table 19. As in the case of the tensile strength, the Type A and Type C composite materials demonstrate a somewhat higher compressive strength level at 2200°F than at room temperature. The high compressive strength demonstrated by the Type B material may be attributed to the relatively coarse texture of the matrix material.

Table 19
COMPRESSIVE STRENGTH DATA

Material Type	Wire Dia. mils	Wire Content	Porosity %	Compressive Strength, ksi	
				Room Temp.	Elevated Temp.
Type A	3.5	5 v/o	10	14.9	20.2 (@ 2115°F)
Type B	3.5	5 v/o	13	50.3	23.7 (@ 2220°F)
Type C	2.0	7 v/o	11	17.7	24.1 (@ 2170°F)

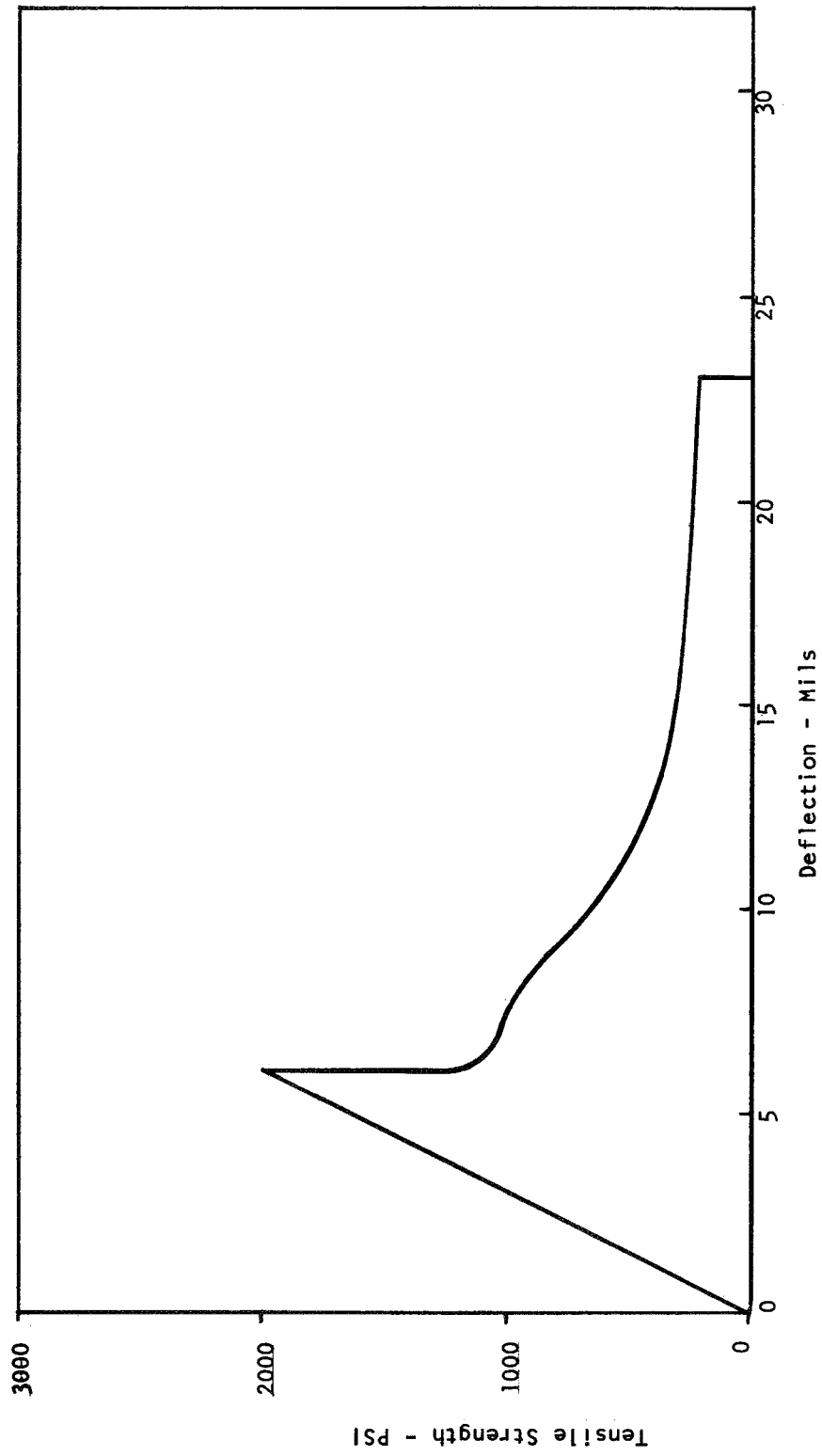


Figure 34. Typical load-deflection curve in room temperature tensile testing Type C composite material.

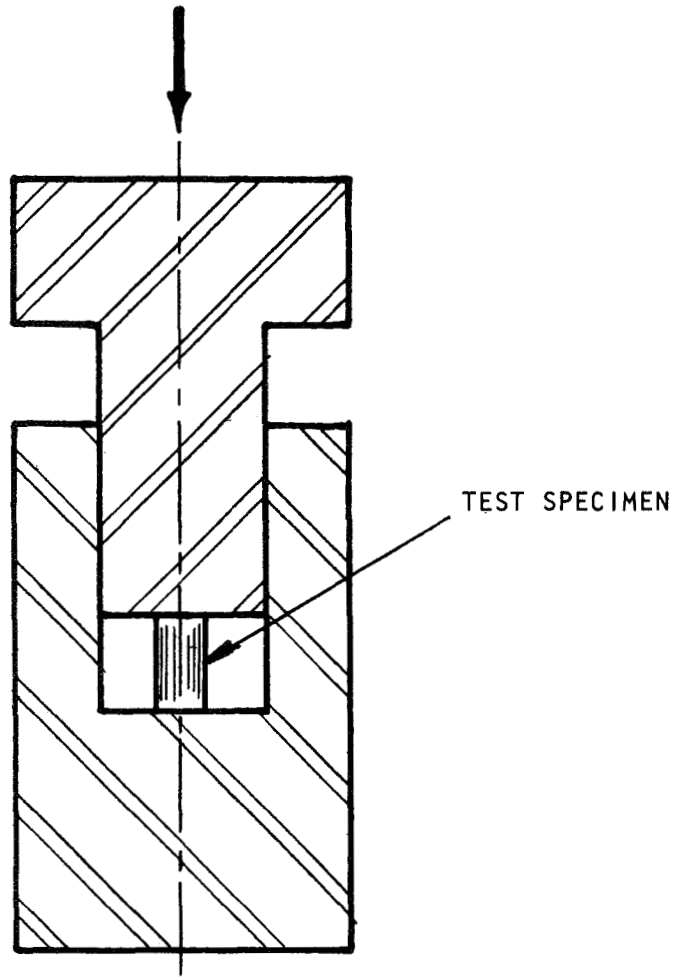


Figure 35. Fixture used for Compressive Strength Testing of Zirconia Composite Materials, Actual Size.

D. Elastic Modulus

The elastic modulus of the Type A, B, and C composites were determined at room temperature by a pulse echo technique using an Elastomat with the specimen resonated in a flexure mode. A specimen of 1/2 inch diameter by 5 inch in length was used for this test. Data interpretation was complicated because the resonant frequencies of these composites were not as clearly defined as they generally are in monolithic materials. Nonetheless, by measuring both transverse and longitudinal pulses, a determination of the elastic modulus of the materials could be obtained. The results of these tests are summarized in Table 20.

TABLE 20
ELASTIC MODULUS OF REINFORCED ZIRCONIA COMPOSITES

<u>Composite Material</u>	<u>Density g/cc</u>	<u>Porosity</u>	<u>Elastic Modulus, psi</u>	
			<u>Longitudinal</u>	<u>Transverse</u>
Type A	5.9	8%	14.8×10^6	16.7×10^6
Type B	5.4	15%	1.4×10^6	1.4×10^6
Type C	5.8	12%	6.7×10^6	8.8×10^6

In addition to these tests, it was planned to obtain a measure of the elevated-temperature elastic modulus of these materials from the tensile test data. However, because of the low tensile loads encountered in the elevated-temperature tests, no meaningful modulus data could be obtained. The only modulus value obtained during the tensile tests was for the Type C material at room temperature. This value of 0.37×10^6 psi is less by about a factor of 20 than the value determined by the pulse echo technique. As postulated before, this behavior may be due to microcracks existing in the specimens. Such localized points of weakness could be expected to have more effect in a tensile test than in a dynamic pulse test that measures the overall vibration mode of a specimen.

E. Thermal Conductivity

Thermal conductivity of the Types A, B, and C composites were conducted on this program by the Dynatech Corporation, Cambridge, Massachusetts. These tests were performed by measuring the temperature drop across the composite specimen which was placed in the apparatus adjacent to a Pyroceram standard. Tests were conducted at a series of temperatures from close to room temperature to 2000°F. The high temperature measurements were complicated by a reaction between the zirconia composite and the Pyroceram standard. Although this did not effect the accuracy of the results, it did necessitate remachining the standards for each run.

The results of these tests are tabulated as follows:

Temperature °F	Thermal Conductivity $\frac{\text{BTU-Ft}}{\text{Hr-Ft}^2\text{°F}}$		
	Type A	Type B	Type C
212	3.12	1.67	2.26
392	2.78		
572	2.37	1.51	2.08
752	1.97		
932	1.74	1.43	1.91
1112	1.62		
1292	1.62	1.43	1.85
1472	1.62	1.52	
1652	1.68		1.79
1832	1.74	1.61	
2012	1.91		1.79

At high temperature, there is not much difference in the thermal conductivity of the three types of composites. At lower temperatures, however, nearly a factor of 2 exists between Type A and Type B for example. This lower thermal conductivity of the Type B composite would contribute to this material being more thermal shock sensitive. This may help explain the generally inferior performance of this material in tests described in the Task 4 portion of this report.

F. Thermal Expansion

The coefficient of thermal expansion of three composite materials, Types A, B, and C, was computed from the heating expansion curves up to 2450°F and extrapolated to 4000°F. The tests were performed by Zircoa on a HARROP automatic recording dilatometer equipped with a Pt wound furnace and using an argon atmosphere.

TABLE 21

Thermal Expansion Determinations

<u>Material</u>	<u>Temperature Range, °F</u>	<u>Thermal Expansion, in/in/°F</u>
Type A	200 to 2450	1.3×10^{-6}
	200 to 1470	2.4×10^{-6}
	200 to 4000	3.9×10^{-6}
Type B	200 to 2450	5.4×10^{-6}
	200 to 4000	5.5×10^{-6}
Type C	200 to 2450	4.7×10^{-6}
	200 to 4000	5.1×10^{-6}

The thermal expansion heating curves of these three materials are presented in Figure 36. The curve of the composite fabricated with the F410 matrix (Type A) exhibits very low expansion in the under 2000°F range. This behavior is attributed to a lattice relaxation phenomenon occurring in the 1000°F range, as well as the phase change which occurs in this partially stabilized material. The heating curves of the 2.85% MgO-stabilized zirconia matrix materials do not exhibit the lattice relaxation phenomenon nor do they show the effects of the monoclinic-tetragonal phase inversion.

This behavior was surprising, particularly in view of the fact that a major rationale in choosing the MgO-stabilized systems for incorporation into this program was based on their unique thermal expansion curves (refer to Figure 2). Although the approach has proven valid on an empirical basis in that improved materials have been developed, it is clear that many of the factors involved in zirconia technology, particularly with regard to reinforced composites, are still not completely understood.

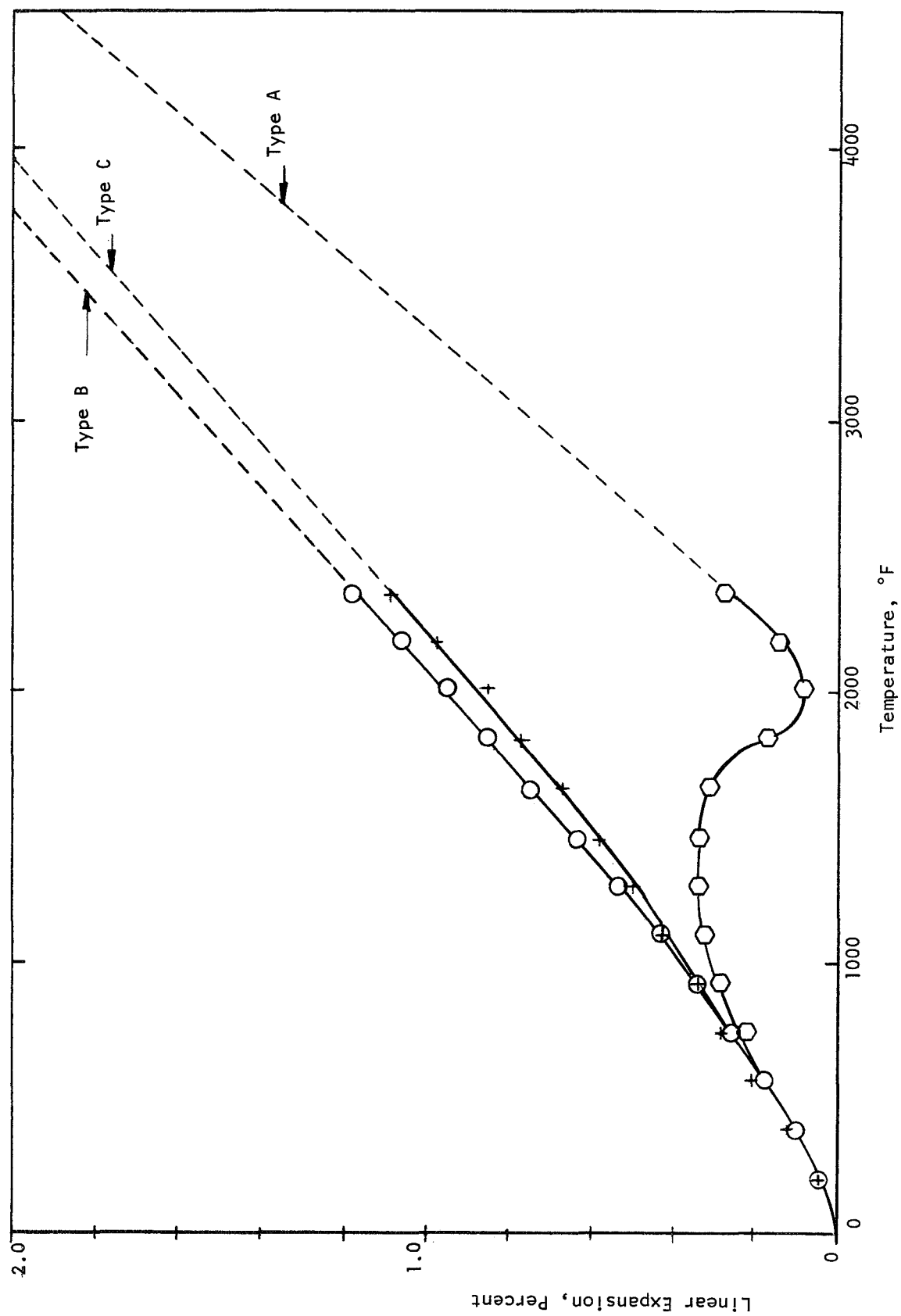


Figure 36. Thermal expansion curves of wire-reinforced zirconia composite materials.

TASK 4 - OXIDATION TESTS

In addition to thermal shock, the other severe condition encountered in rocket nozzle environments is the chemical reactivity of the combustion products. With the liquid propellant system being considered here, a highly oxidizing environment exists. Therefore, this part of the program was aimed at evaluating the three zirconia composites under consideration (Types A, B, and C) with respect to this type of environment.

This task was comprized of two series of oxidation tests. The first test series consisted of an exposure of the composite materials to the exhaust products of a rocket engine at 4200°F. The second series, an air oxidation test, was performed at 3000°F in a simulated air mixture using a plasma jet heat source.

A. Rocket Engine Exhaust Test

The rocket engine exhaust tests were performed by TRW Systems at the Capistrano Test Site, Capistrano, California on the High Energy Propellant Test Stand. A 500-pound thrust water-cooled engine was used for these tests with a propellant combination of $N_2O_4/50\%N_2H_4-50\%UDMH$ at a mixture ratio of 1.6 to 1.

1. Test Plan and Procedure

Specimens of the three composite materials were to be tested in the exhaust gas stream at a temperature of 4200°F for periods of 100, 200, and 400 seconds. An additional specimen of the most promising material was to be subjected to an 800-second exposure.

The test scheme and specimen shape is illustrated in Figure 37. The test specimen was placed in the engine exhaust so that it was exposed to the exhaust gases at the specified temperature. The test engine is shown in Figure 38a with the test specimen retracted. Figure 38b shows the test specimen rotated into position under the rocket engine nozzle. During the performance of actual tests, the test specimen was not rotated into position until the engine was started and had reached equilibrium operating conditions.

Specimen temperatures were monitored and recorded during the test by a two-color optical pyrometer mounted on the test stand. The specimen surface reached a temperature between 4100 and 4200°F almost instantaneously and then remained constant throughout the test cycle.

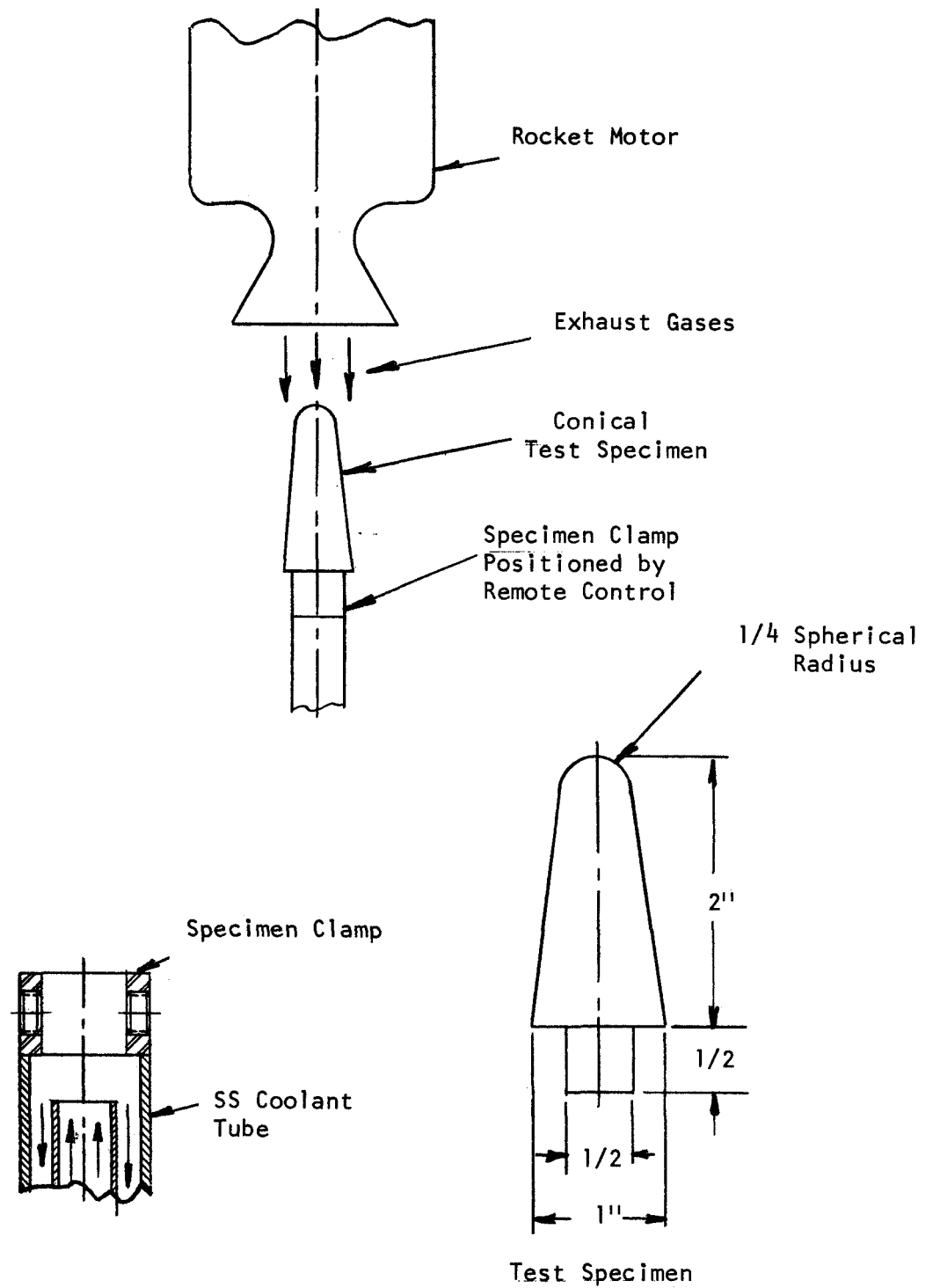


Figure 37. Test scheme and specimens used for propellant exhaust oxidation tests of reinforced zirconia composites.

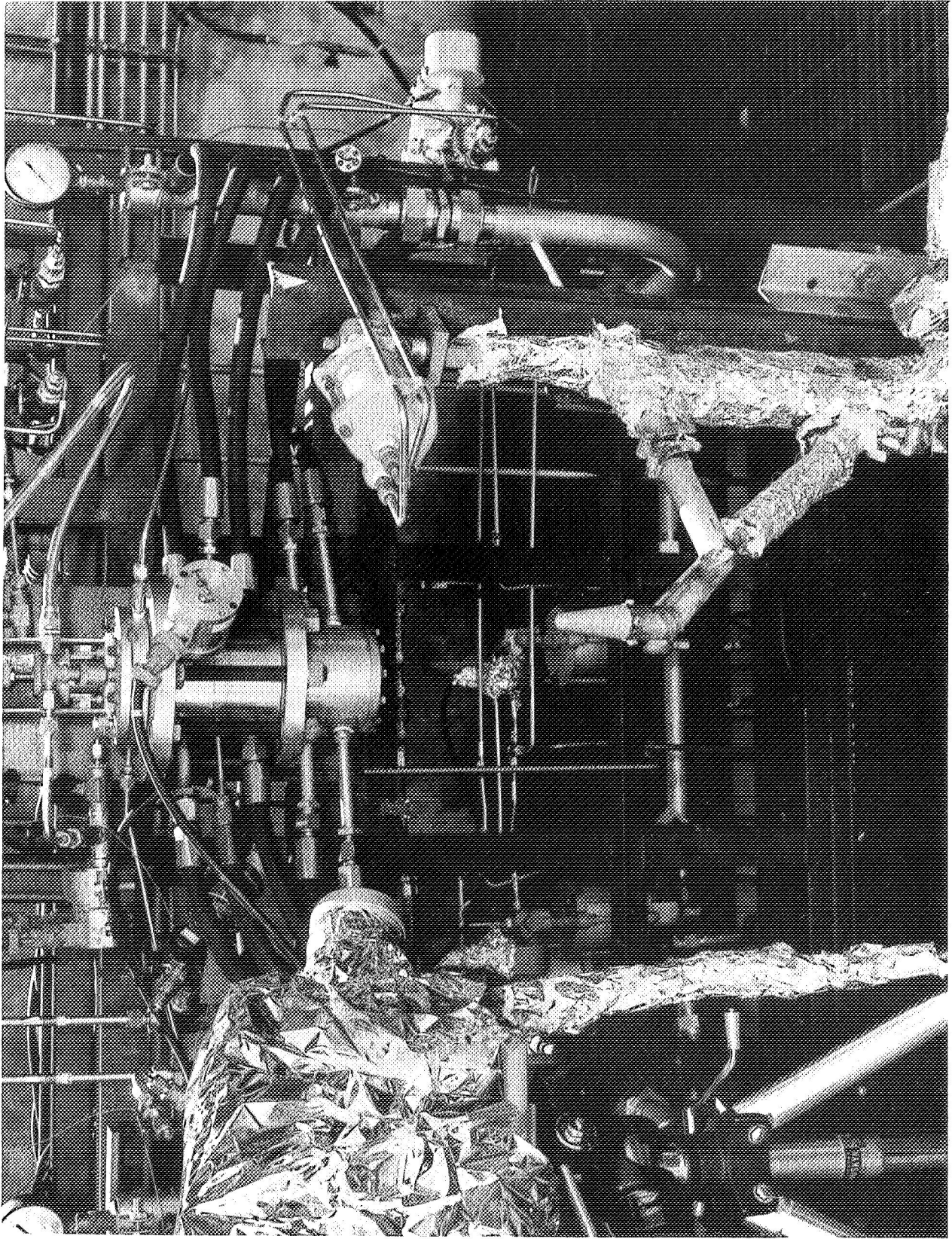


Figure 38a. The 500 pound thrust engine used for propellant oxidation tests. Specimen is mounted in pretest position ready to be rotated into

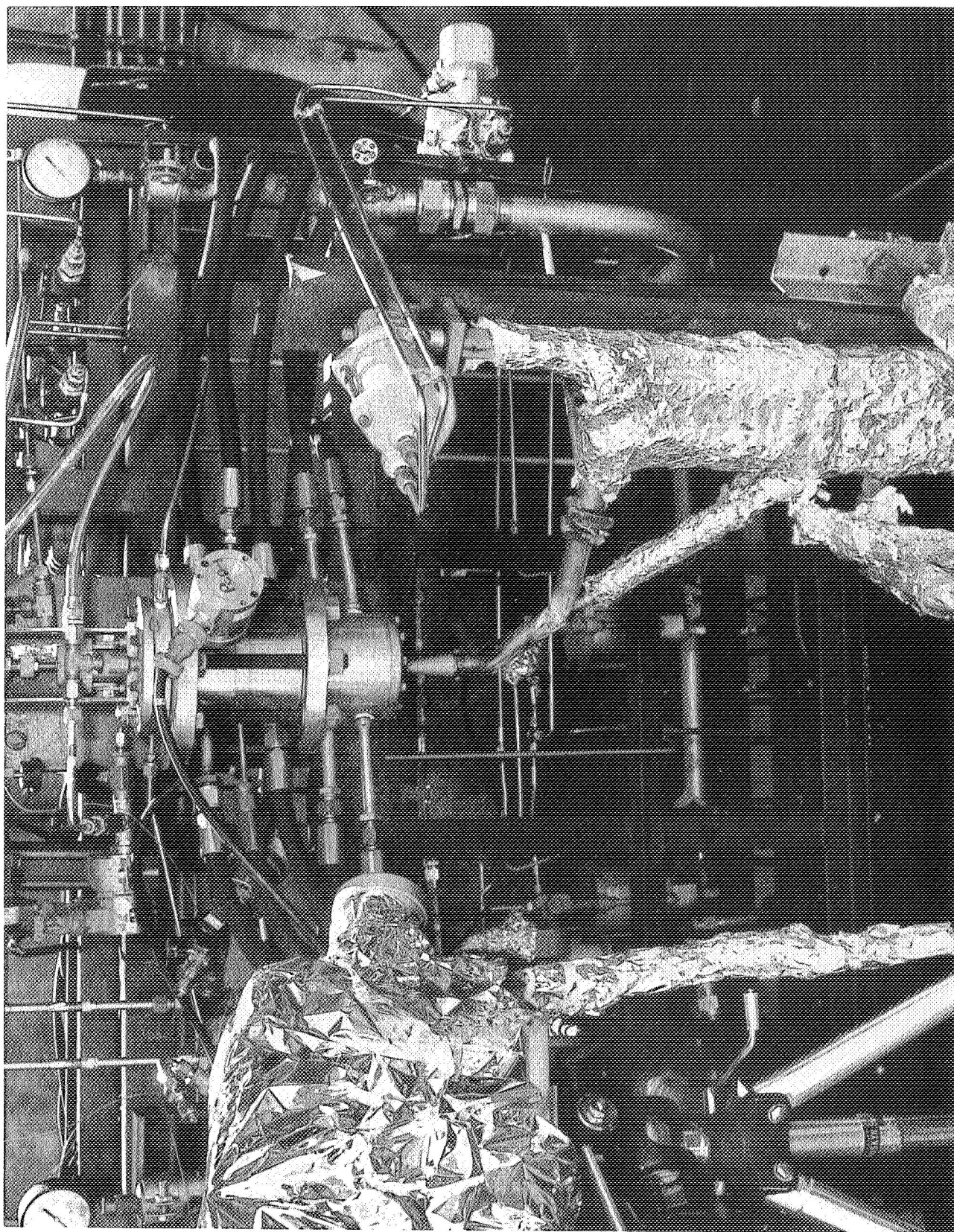


Figure 38b. The 500 pound thrust engine used for propellant oxidation tests. Shown with test specimen rotated into test position.

2. Test Results

The test specimens prior to testing are presented in Figure 39. The composites fabricated with 2-mil diameter wire exhibit a more uniform surface and greater freedom from fissures and surface cracks than composites incorporating larger wire diameters. This phenomenon is related to the fact that the coefficient of expansion mismatch between composite components is less detrimental when smaller wire diameters are employed. Petrographic examinations, carried out by Zircoa, also indicated composites reinforced with 2-mil diameter wire had lower residual stress levels than composites fabricated with 3.5 mil or larger wire diameters.

The propellant oxidation test results are summarized in Table 22 and the appearance of the specimens after testing is presented in Figures 40 and 41. The test results can be correlated to the visual appearance of the specimens before testing and to a lesser extent to porosity. Composite material Type C which showed the greatest freedom from surface cracks before testing, demonstrated superior erosion resistance in this test. The type B composite, formulated with medium-texture zirconia powder and containing a number of surface cracks as-machined, suffered the greatest degree of erosion of the 3 composite materials tested. The use of medium-textured zirconia powder in the Type B composite also resulted in greater porosity: 13% as compared to 10% for composites using fine-textured zirconia powder.

Table 22

SUMMARY OF PROPELLANT OXIDATION TEST RESULTS

Composite Type	Composite Composition	Nominal Test Duration			
		100 Seconds	200 Seconds	400 Seconds	800 Seconds
A	F410 Matrix, 5v/o, 3.5 mil dia. wire.	100 Seconds. Intermediate erosion.	200 Seconds. Intermediate erosion.	58 Seconds. Test aborted; sample broke & was ejected.	- - - - -
B.	2.85% MgO Med. Texture, 5v/o 3.5 mil dia. wire.	100 Seconds. Severe erosion.	200 Seconds. Severe erosion.	400 Seconds. Severe erosion.	- - - - -
C.	2.85% MgO Fine Text., 7v/o 2-mil dia. wire.	100 Seconds. Very little erosion	160 Seconds. Aborted test; engine failure. Very little erosion.	400 Seconds. Very little erosion.	800 Seconds. Very little erosion.

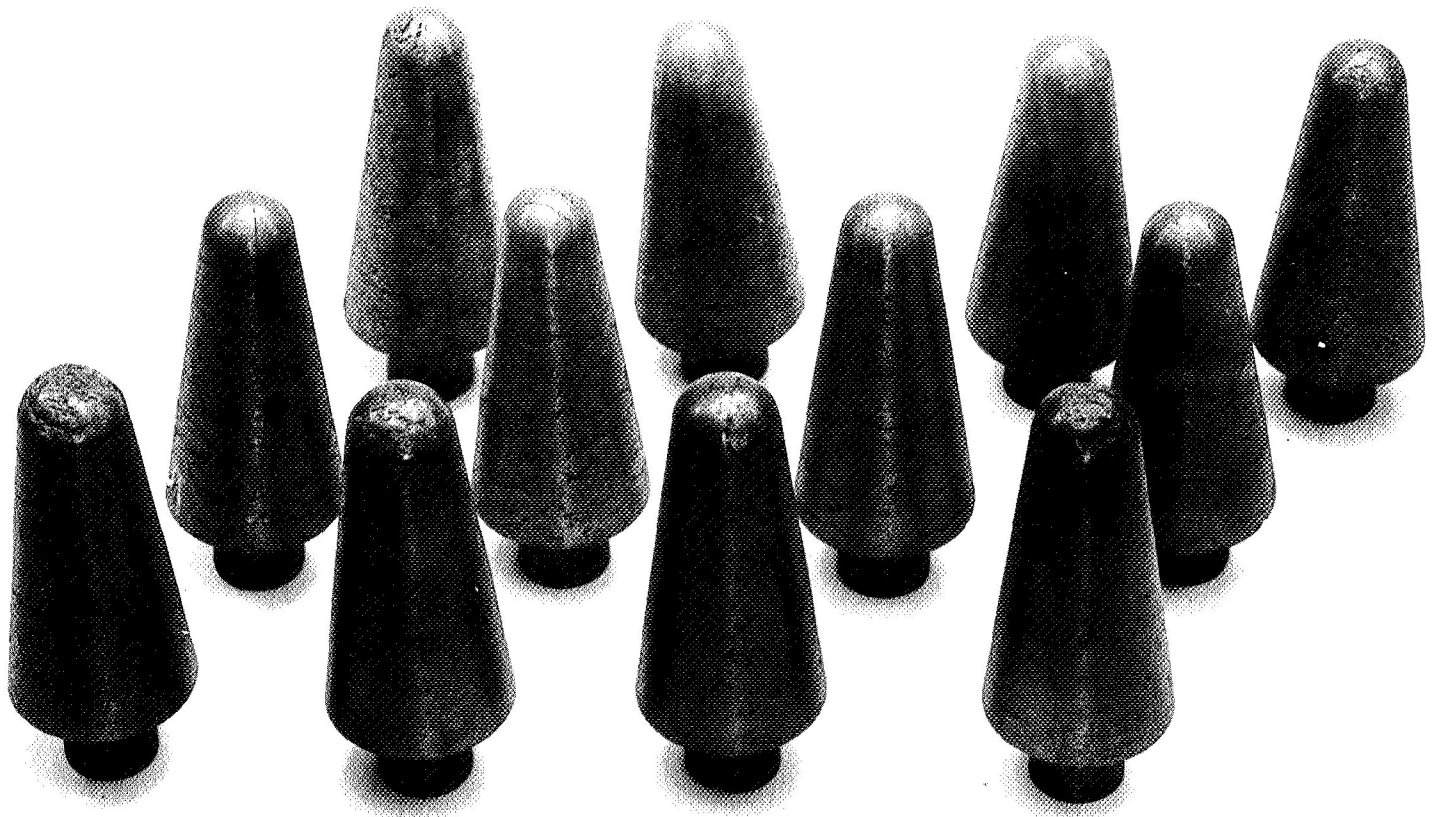


Figure 39. Reinforced zirconia composite specimens for rocket engine exhaust tests prior to testing.

Type C - Top Row - 2.85% MgO fine-texture matrix reinforced with 7v/o of 2.0 mil diameter W-3%Re wire.

Type B - Center Row - 2.85% MgO medium-texture matrix reinforced with 5v/o of 3.5 mil diameter W-3%Re wire.

Type A - Bottom Row - F410 fine-texture matrix reinforced with 5v/o of 3.5 mil diameter W-3%Re wire.

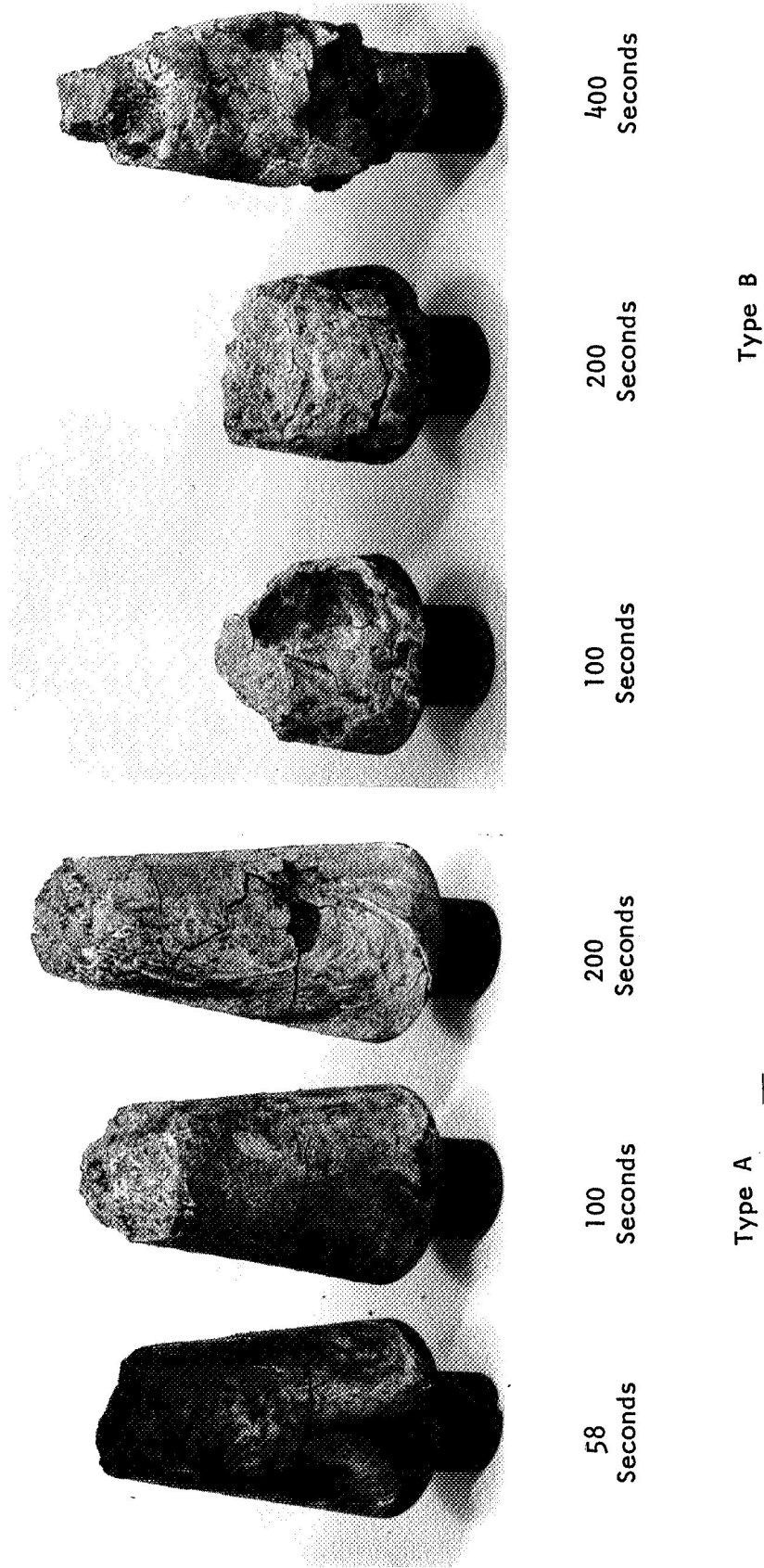
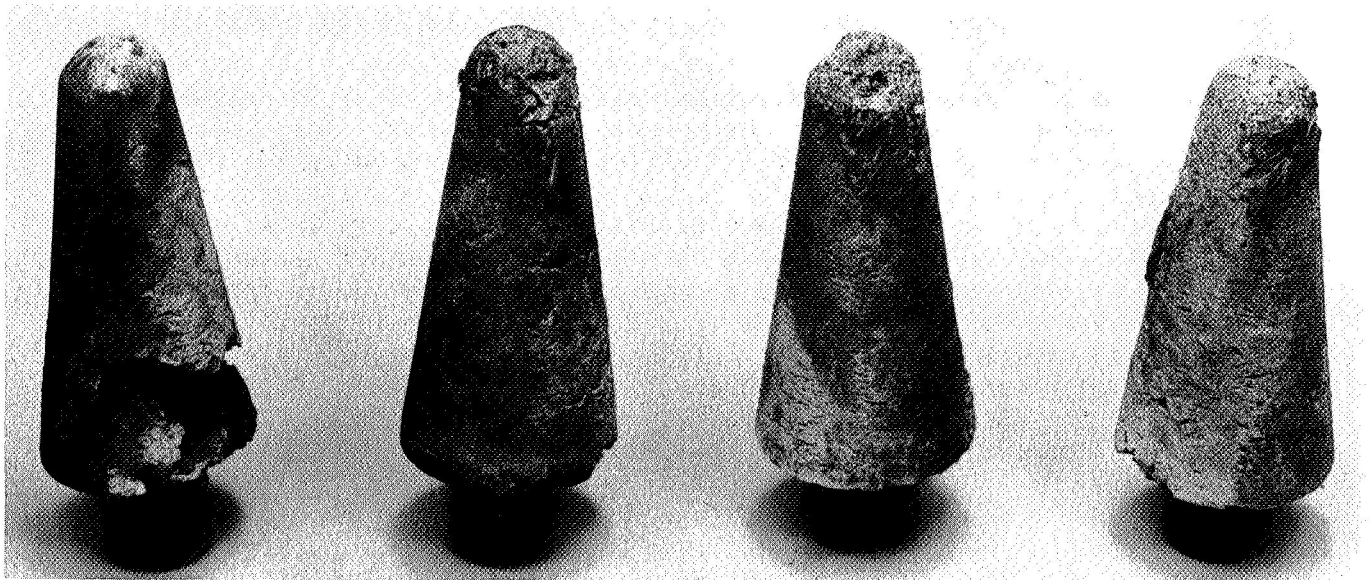


Figure 40. Specimens of Type A and Type B reinforced zirconia composites after rocket engine exhaust tests of various durations as indicated.



100
Seconds

160
Seconds

400
Seconds

800
Seconds

Figure 41. Specimens of Type C reinforced zirconia composite after rocket engine exhaust tests of various durations as indicated.

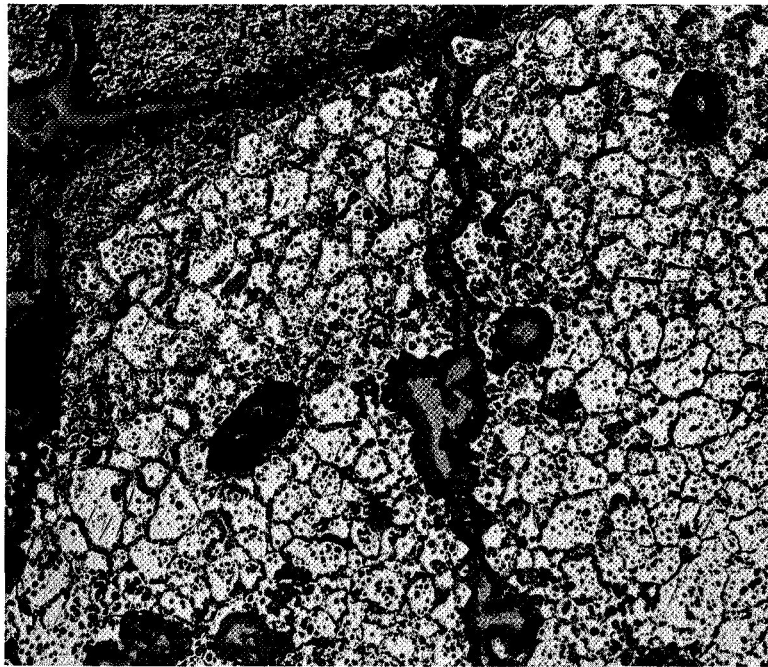
The erosion mechanism appears to operate through failure of the supporting fibers which allows pieces of the composite material to be sheared and carried off by the high velocity gas stream. The loss of relatively large pieces was most obvious during the course of the testing of the Type B material.

Analysis of the selected oxidation-tested specimens was performed by metallographic, electron microprobe, and petrographic analyses.

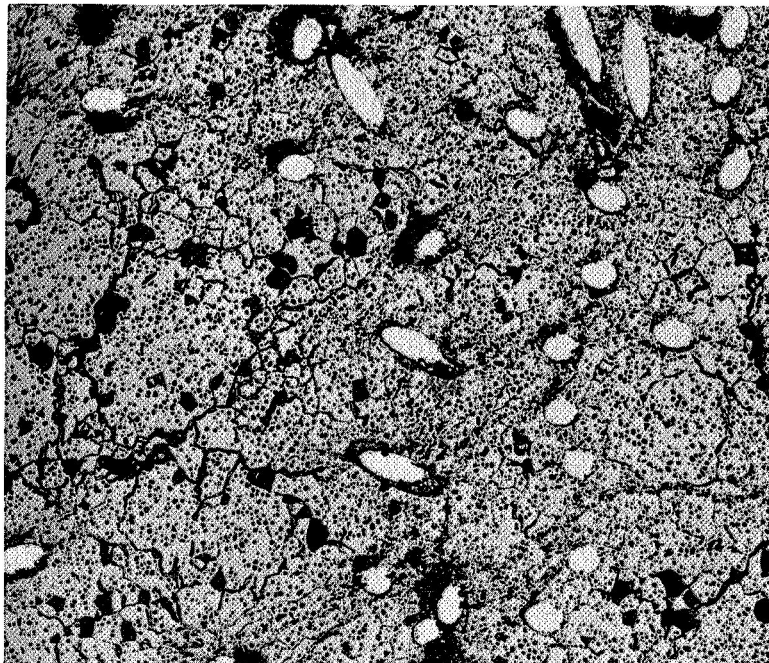
Metallography - The major microstructural features of all three types of composite specimens after oxidation testing were similar in nature but varied in degree in relation to the duration of the test. The typical behavior of these specimens during oxidation testing is illustrated by the 800-second Type C composite specimen shown in Figure 42. Figure 42a illustrates the microstructure at the outer surface nearest to the exhaust flame. The reinforcing wires in this area have been completely removed either by oxidation or dissolution into the zirconia matrix. The spongy appearance of the grain boundaries is indicative of diffusion of W into the zirconia matrix prior to its removal by oxidation. This type of microstructure extends to a depth of approximately 1/4 inch below the surface. The microstructure of the interior of the specimen, Figure 42b, appears to be unaffected by the test except for a tendency to form microcracks.

The depth of wire depletion as a function of duration of test exposure is of interest to help understand the mechanism of degradation and to help extrapolate the behavior of this material to longer times. Because the Type A and B composites suffered considerable material loss by erosion during the test, a meaningful plot of this relationship could not be made. For the Type C material, which remained virtually intact after the test, the relationship between depth of wire degradation and test time is shown in Figure 43. In this plot, the depth is plotted as a function of the square root of time. Except for the 160-second datum point, a straight-line relationship is observed. This indicates that the deterioration of the material is a diffusion-controlled process as would be expected. The data also indicate, therefore, that subsequent increments of deterioration will require longer and longer exposure times. This is a promising trend for longer-time applications of this material.

Electron microprobe analysis - The 800-second Type C composite metallographic specimen was also analyzed by electron microprobe analysis. With the apparatus set to detect tungsten, the electron beam was moved inward from the exposed surface of the specimen. As the beam passed over a tungsten wire, the appropriate machine read-out chart would momentarily indicate about 100% W instead of the normal near-zero background indication. The resultant distance-versus-tungsten content plot is shown in Figure 44. This chart indicates that the tungsten was virtually completely removed for about 150 mils from the edge of the specimen.



(a)



(b)

Figure 42. Cross-section of Type C reinforced zirconia specimen after the 800-second propellant oxidation test showing (a) area adjacent to hot surface and (b) interior area. Magnification 75X

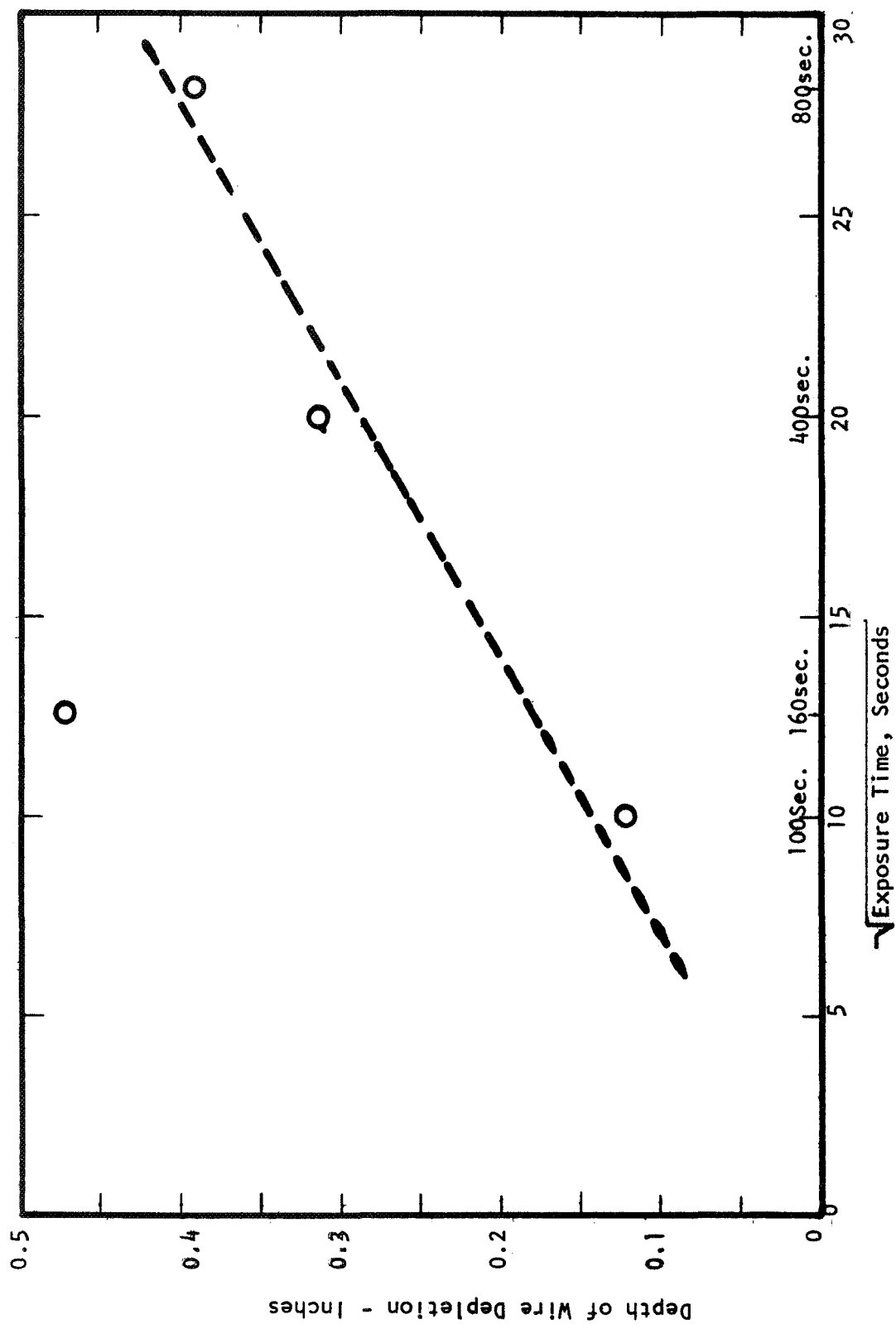


Figure 43. Wire Depletion Depth as a Function of Test Duration for Type C Composite Propellant Oxidation Specimens.

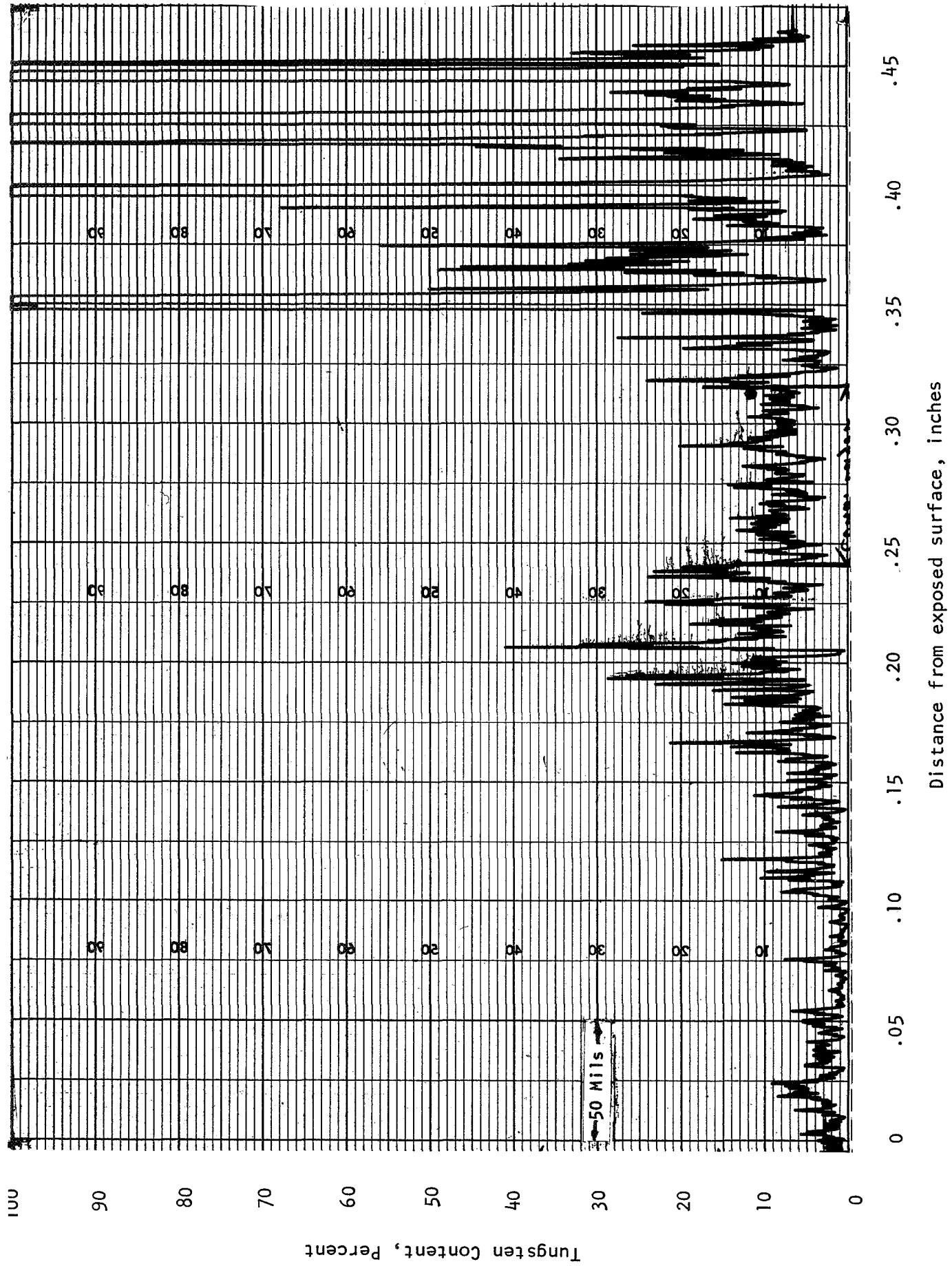


Figure 44. Electron microprobe W scan of Type C composite specimen after 800 seconds exposure in the probellant oxidation test.

The chart then indicates an intermediate zone with an increased tungsten content. The relatively uniform tungsten level in this zone indicates that the tungsten from the wires has diffused into the zirconia matrix. At about 350 mils from the surface, the intermittent tungsten signals, indicative of the as-fabricated composite, are evident. Similar scans of the same area with the machine set to detect zirconium and oxygen were performed. These scans gave no indications of other interactions taking place within this material.

Petrography - Selected oxidation-tested specimens were examined by Zircoa by petrographic techniques. For this examination, specimens were prepared in thin sections which were then polished on both faces so that they could be viewed by transmitted light. This technique allowed the observation of general microstructural features, phase relationships, and the extent of residual stress existing within the material.

The specimens studied by this technique included a Type A and a Type B composite each oxidation-tested for 200 seconds, and two Type C samples tested for 160 and for 800 seconds. These four samples exposed to oxidizing environments at 4200°F all showed similar general features. The hot face of the material was destabilized to a depth of about 2 mils due to volatilization of the MgO out of the solid solution (Figure 45). The tungsten wires are completely removed from the surface layer, and for a short distance back into the ceramic. The intermediate zone back from the surface contains partially eroded tungsten-wires, each of which is encapsulated in a layer of destabilized zirconia (Figure 46). There is good evidence of residual strain in the ceramic in a narrow zone immediately back of the hot face. The zirconia in the hot face shows that the oxidation and volatilization of the tungsten wires is occurring by a reaction with the zirconia. The durability of the composite may have been due to the destabilization-oxidation reaction, the rate of which appears to have been governed by a diffusion process in the solid state. This would probably result in slower reaction rates than if the process were governed by diffusion in the gas state through open fissures as might be expected in the coarser materials.

The following conclusions have resulted from the petrographic analysis of these four specimens:

1. The tungsten is removed only from the area near the surface of the specimen which is exposed to the oxidizing environment at 4200°F
2. The surface material undergoes a slight destabilization due to the volatilization of the MgO. In some instances a thin film of monoclinic zirconia can develop on the surface. In some instances, destabilization of the ceramic can occur along grain boundaries (See Figure 47).



Figure 45. Cross-section of hot face of Type A material, F410 + 5v/o of 3.5 mil wire, propellant oxidation specimen after 200 seconds exposure at 4200°F. Transmitted polarized light, 370X.



Figure 46. Cross-section of intermediate zone Type A material, F410 + 5v/o of 3.5 mil wire, propellant oxidation specimen, after 200 seconds exposure at 4200°F; transmitted polarized light, 150X.

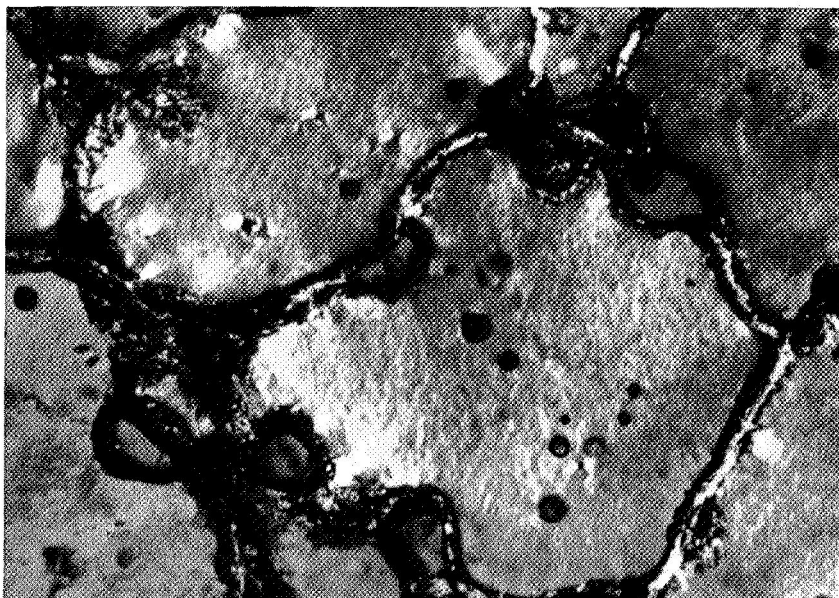


Figure 47. Interior of Type A zirconia composite after rocket engine propellant oxidation tests showing destabilization along zirconia grain boundaries; transmitted polarized light, gypsum retardation plate, 370X.

3. The ZrO_2 -MgO solid solution immediately adjacent to the tungsten wires will destabilize at a high temperature. This forms a capsule of monoclinic ZrO_2 around each wire in the intermediate zone.
4. The surface ZrO_2 recrystallizes rapidly at temperatures as high as 4200°F, with noticeable effects occurring within 200 seconds.
5. The cubic zirconia phase immediately back of the recrystallized zone is strained due to the thermal stresses induced by the rocket exhaust test.

3. Conclusions From Engine Exhaust Testing

In addition to yielding an understanding of the oxidation behavior of these composites, the rocket engine exhaust tests provided a discriminating and decisive measure of the relative merit of the Type A, B, and C materials for use in throat insert fabrication. Based on overall appearance, erosion resistance, and general structural integrity after oxidation testing (see Figures 40 and 41), the Type C composite was clearly the superior material. The overall merit of these materials for throat insert fabrication were rated in decreasing order as follows:

<u>Composite Designation</u>	<u>Zirconia Matrix Material</u>	<u>Reinforcement (W-3%Re Wire)</u>
Type C	2.85% MgO Fine-Texture	2.0 mil, 7 v/o
Type A	F410	3.5 mil, 5 v/o
Type B	2.85% MgO Medium-Texture	3.5 mil, 5 v/o

These rocket engine exhaust tests offered probably the most realistic environment of any test in this program for overall evaluation of these materials for rocket nozzle application. Therefore, the above rating was the primary consideration in choosing the composite for fabrication of inserts for test firing in Task 5 of the program.

B. Air Oxidation Tests

It was desired to know the behavior of these composites in an environment other than the specific rocket engine exhaust environment of primary interest to this program. Such information would yield a

better general understanding of these composites which can aid in their more intelligent use both in this specific rocket nozzle application and possibly in other places such as jet engines, where high temperature materials are required. In light of this combined purpose, a 3000°F exposure in moving air was chosen as an appropriate test condition.

1. Test Procedure

The air oxidation tests were carried out by heating the test specimen to 3000°F by a plasma jet torch using a simulated air mixture of N₂ and O₂. The test was performed at the TRW Materials Laboratory using a 40KW Plasma Torch with a Metco plasma gun. The specimen was a 1-inch diameter x 1/4" thick disc.

The test was performed by placing the specimen in a specially built air oxidation furnace, shown schematically in Figure 48. The furnace chamber was a 3-inch diameter x 3-inch long cavity machined in a zirconia block. The gas inlet and outlet ports were located tangentially to impart a swirling motion to the gas and uniform exposure to the specimen surfaces to the test conditions.

Temperatures were monitored by a thermocouple. All testing was carried out in air with no protective atmosphere. Timing of the test was started when the specimen reached 3000°F and test conditions were held constant for the duration of the time cycle. Specimens were removed from the furnace and allowed to cool in still air at the completion of the test. The 3 composite materials were each tested for 4 time periods of 3, 6, 10, and 30 minutes (for a total of 12 specimens).

2. Test Results

The data from the air oxidation tests are summarized in Table 23. A slight weight gain was recorded for all the specimens. Since the high temperature form of tungsten oxide (WO₃) is gaseous at the test temperature of 3000°F, most of the weight change of the specimens occurred during the cool down portion of the cycle and is, therefore, of uncertain significance. The volume change, also attributed to the formation of tungsten oxide, is correspondingly of limited significance.

Metallographic examination of the oxidation tested specimens showed the presence of a reinforcement wire depletion zone at the exposed surfaces. Typical microstructures of the composite specimens after a 3 and 30 minute exposure are presented in Figure 49. The depth of the depletion zone, as indicated in Table 23, depended on the duration of the test. These data are plotted in Figure 50 with the depth of deterioration shown as a function of the square root of the test duration. The Type C material conforms reasonably well to the diffusion-controlled mechanism implied by this type of plot. The Type A and Type B material indicate a faster initial degradation rate, but then they showed a change in behavior that results in a slower rate of wire deterioration.

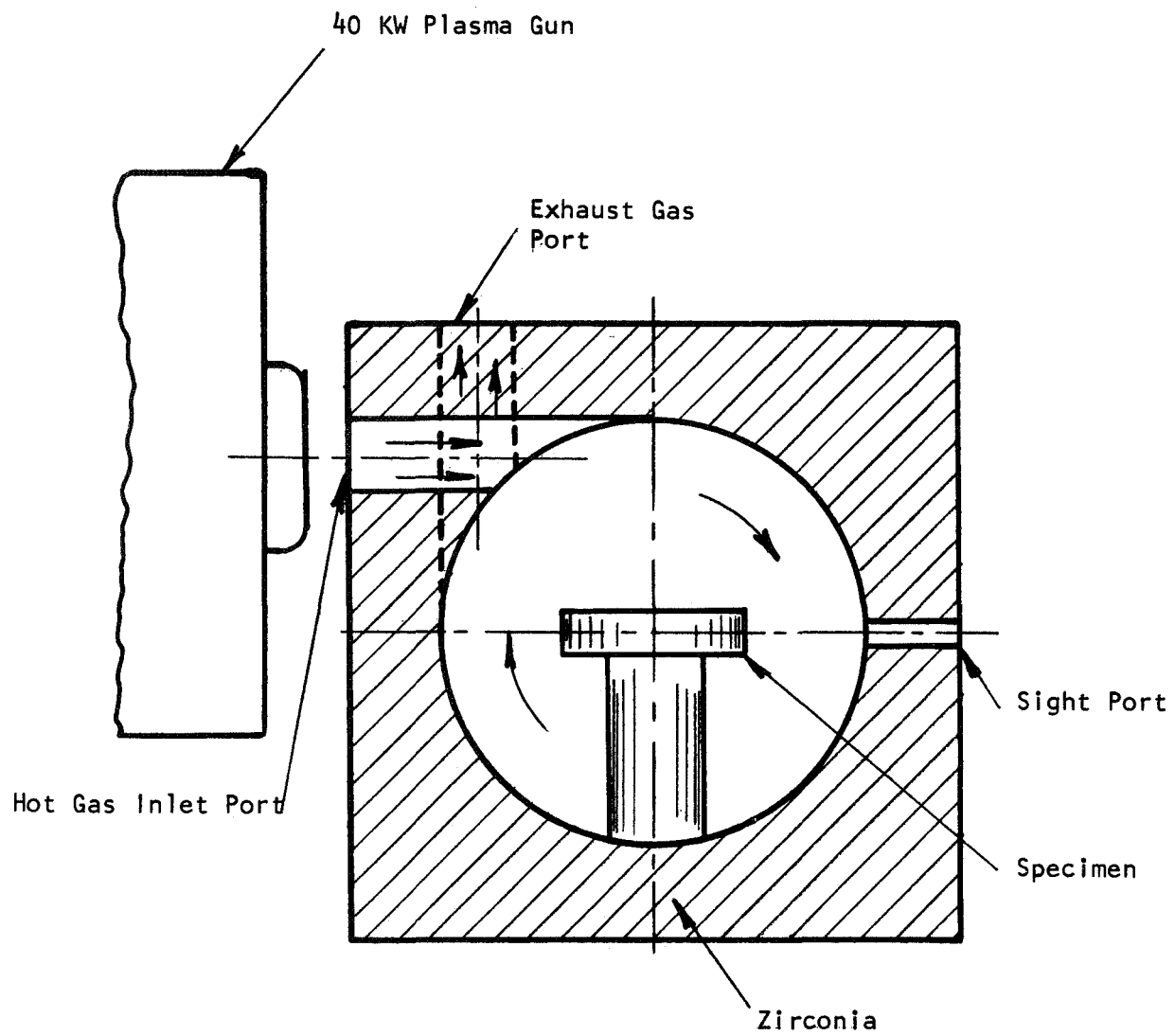
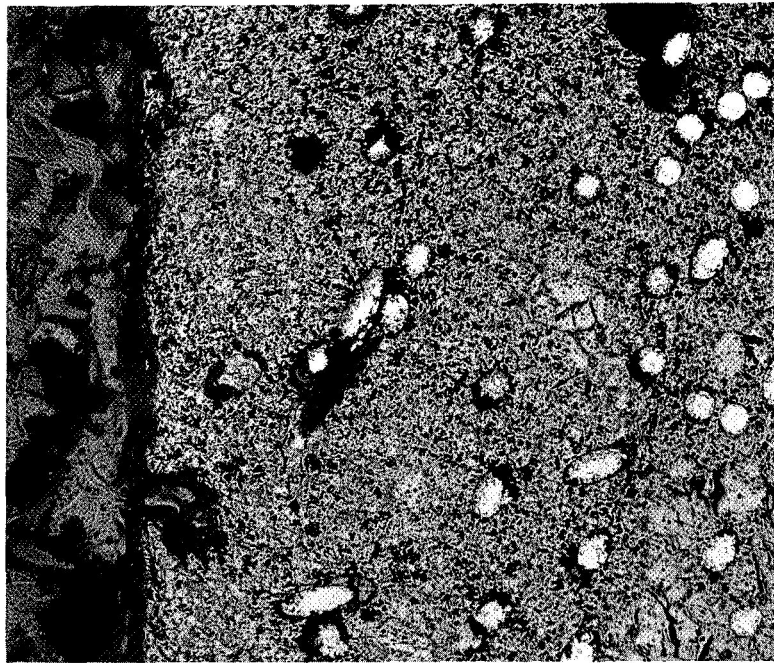


Figure 48. Test scheme for air oxidation tests of reinforced zirconia composites.

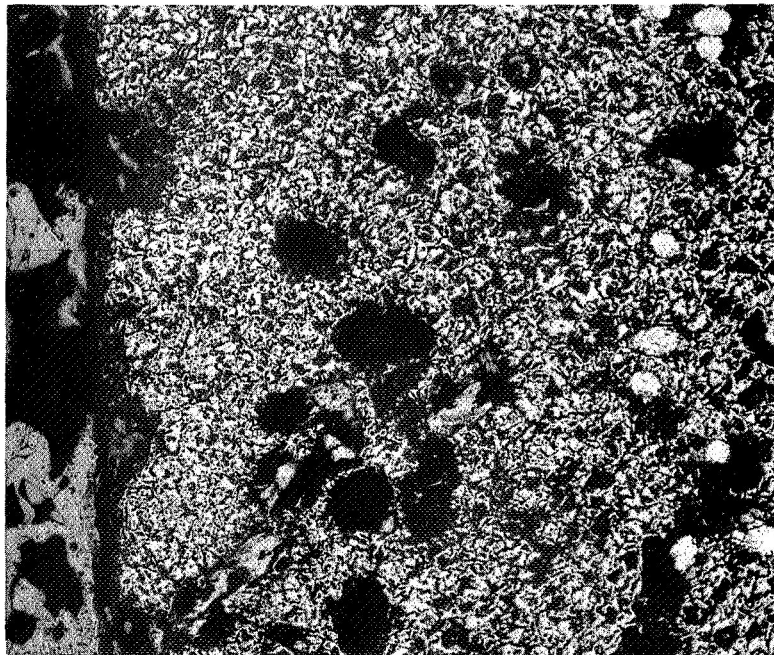
TABLE 23

AIR OXIDATION TEST DATA

Material Type	Zirconia Matrix Material	Wire Diameter, mils	Wire Content, %/O ₂	Porosity, %	Test Duration, Minutes	Volumetric Gain, %	Wt. Gain, %	Depth of Deterioration, mils
Type A	F410	3.5	5	10	3	5.0	1.25	17
"	"	"	"	"	6	5.0	1.08	20
"	"	"	"	"	10	5.0	1.08	25
"	"	"	"	"	30	6.4	0.75	26
Type B	2.85% MgO Medium Texture	3.5	5	13	3	3.5	1.30	25
"	"	"	"	"	7	7.5	1.85	40
"	"	"	"	"	10	7.5	1.54	40
"	"	"	"	"	30	9.0	1.97	46
Type C	2.85% MgO Fine Texture	2.0	7	11	3	4.2	1.18	11
"	"	"	"	"	6	6.5	1.56	15
"	"	"	"	"	10	6.8	1.67	26
"	"	"	"	"	30	9.0	1.57	37



(a) 3 Minute Exposure 75X



(b) 30 Minute Exposure 75X

Figure 49. Cross-section views showing hot surface of Type C composite material after exposure at 3000°F in air-oxidation tests for (a) 3 minutes and (b) 30 minutes.

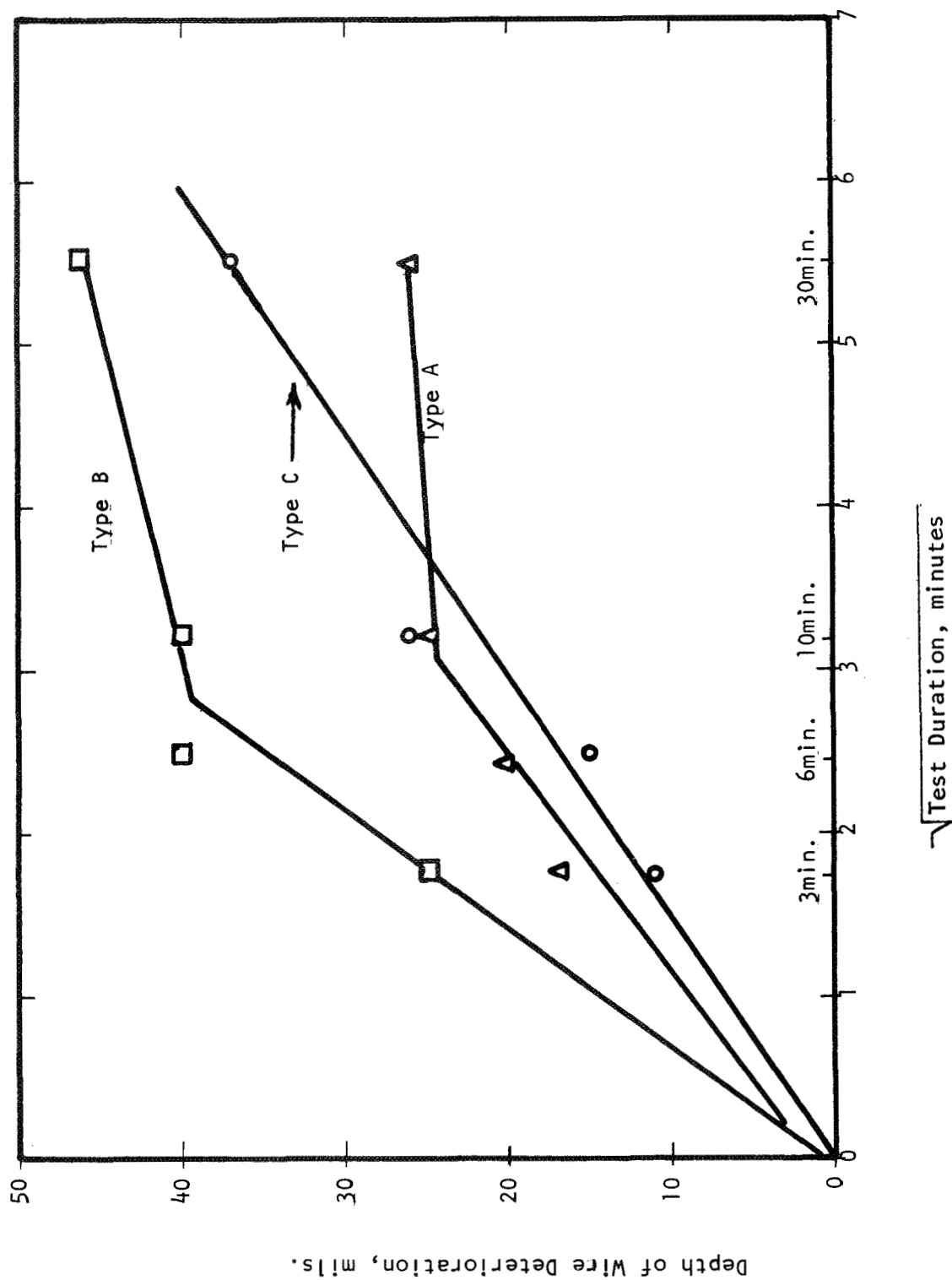


Figure 50. Effect of Test Duration on Depth of Wire Depletion of Composites During a 3000°F Air-Oxidation Test.

These specimens are porous and they have a tendency to form microcracks. This precludes any simple analysis of these data. Further, the porosity and microcracking tendency varies with the different types of material. In general, the Type C material, reinforced with the 2-mil wire, has less tendency to form microcracks than do the composites reinforced with 3.5-mil wire. This may account for its lower initial oxidation rate. The highest porosity was in the Type B material, and this material showed the highest oxidation rate of the three composites. The tungsten oxide (WO_3) formed from this wire oxidation is gaseous at 3000°F, so it can offer no protection from further oxidation. There was no diffusion of tungsten into the zirconia matrix in these oxidation specimens. The oxidation of these specimens, therefore, must depend on the diffusion of oxygen through the composite to the metal surface. The rate of such attack will, therefore, depend on the combined effects of porosity, microcracks, and the amount of wire surface area that is exposed to such conditions.

TASK 5 - INSERT DESIGN AND FABRICATION

The program to be followed in Task 5 included the design and fabrication of a series of three nozzle inserts with a 3-inch throat diameter to be furnished to NASA for test firing. The first insert was to be fabricated from the composite material that offered the greatest potential as a throat insert as determined by the preceding portion of the program. Following the test firing of the first insert, a second composite insert was to be fabricated incorporating any modifications of design or materials that were indicated by the results of the first test firing. The third insert, containing no reinforcement wire, was to be fabricated with the same matrix material and processing conditions as were used in fabricating the second insert so that a one-to-one evaluation of the effects of the reinforcing wires could be obtained.

A. First Reinforced Insert

For the first insert, a composite material was chosen and a design and accompanying thermal analysis was prepared. The insert was then fabricated and test-fired. Prior to this point in the program, a throat insert essentially of Type A material had been supplied to NASA-Lewis under separate contract, (NAS 3-11265). This insert was also of 3-inch throat diameter of similar design as the one to be produced in this program. In fact, the test firing of these two inserts were carried out concurrently at NASA-Lewis. This allowed a good comparison of the two nozzles. In the following discussion of the nozzles produced in this program, this comparison of performance will be evident.

1. Materials Selection

The selection of a composite material for the first insert was made using the data derived from Tasks 1 through 4 of the program with particular emphasis on the thermal shock and propellant oxidation test results. Based on these data, the composite material selected was Type C, a 2.85% MgO stabilized, fine texture zirconia matrix, reinforced with 7 v/o of 2-mil diameter x 1/8 inch long W-3%Re wire. The decision was facilitated to a degree by the fact that a nozzle of the Type A composite - considered as a second choice on this program - was already being produced and that the test firing results of it would be available for comparison on this program.

2. Design and Thermal Analysis

As an aid to the design of the throat insert and the associated support structure, a preliminary thermal stress analysis was performed on a tungsten wire reinforced insert. The preliminary analysis was performed before completion of Tasks 2 and 3 and was based on limited experimental data and estimated material properties. The results of this analysis revealed that all temperatures would be within established operational limits.

The preliminary analysis expedited the design of the nozzle insert and the associated tooling. When physical property data on the Type C composite material became available, the following analysis, based on current experimental data, was performed.

Configuration - The configuration of the throat insert considered in the analysis is presented in Figure 51. For the thermal stress analysis, it was considered that the throat would be installed in a molded, chopped silica phenolic throat support component. A cylindrical steel shell provided structural support on the O.D. surface. The throat insert assembly analyzed is presented in Figure 52. This configuration is identical with the nozzle of the Type A composite that had been supplied prior to this point in the program.

Material properties - The available physical properties of the materials were reviewed for the analysis. Properties such as thermal conductivity, specific heat, and density are required for the thermal analysis. In addition to these properties, material strength, modulus of elasticity, thermal coefficient of expansion, and Poisson's ratio all as a function of temperature are necessary for the stress analysis. The throat insert was fabricated from 2.95% MgO-stabilized zirconia powder and 7 v/o of 2-mil diameter W-3%Re wire. The only experimental material property data that exists for this composite is what was previously determined during the program. For this analysis, experimental material property values were used where possible. These physical property data are summarized in Table 24 and Figure 53. The physical property data for the molded chopped silica phenolic throat support (MX2646) and the steel support were selected based upon previous TRW experience. These data are the same as that used previously (2) and are presented in Table 25.

Heat transfer analysis - A heat transfer analysis was conducted on the design presented in Figure 52. Only the throat station was analyzed since this station represents the maximum heat flux location. Also the throat insert thickness at this location is a maximum and, thus, represents maximum thermal stress location.

The heat transfer analysis was performed using the TRW Charring Ablative Materials Program. This program solves the heat balance in one dimension using a finite difference technique. For this analysis, a cylindrical coordinate system was assumed. This program is designated TRW Computer Program No. 81520.

The combustion gas properties used were as follows:

Convective Heat Transfer Coefficient = $927 \text{ BTU/hr-ft}^2\text{-}^\circ\text{F}$

Specific Heat = $1.39 \text{ BTU/lb.-}^\circ\text{F}$

Adiabatic Wall Temperature = 4610°F

It was also assumed that no throat erosion would occur.

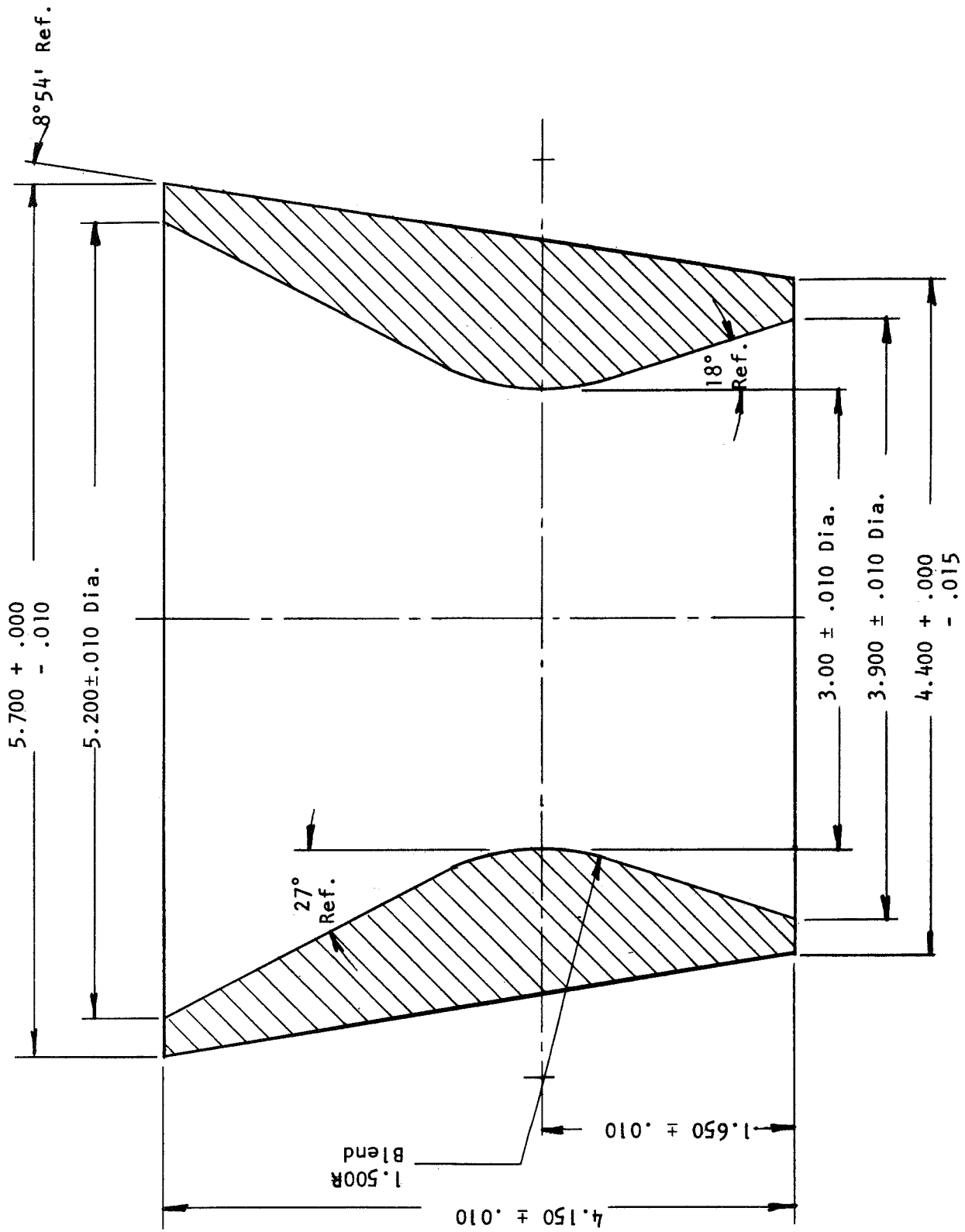


Figure 51. Reinforced zirconia throat insert.

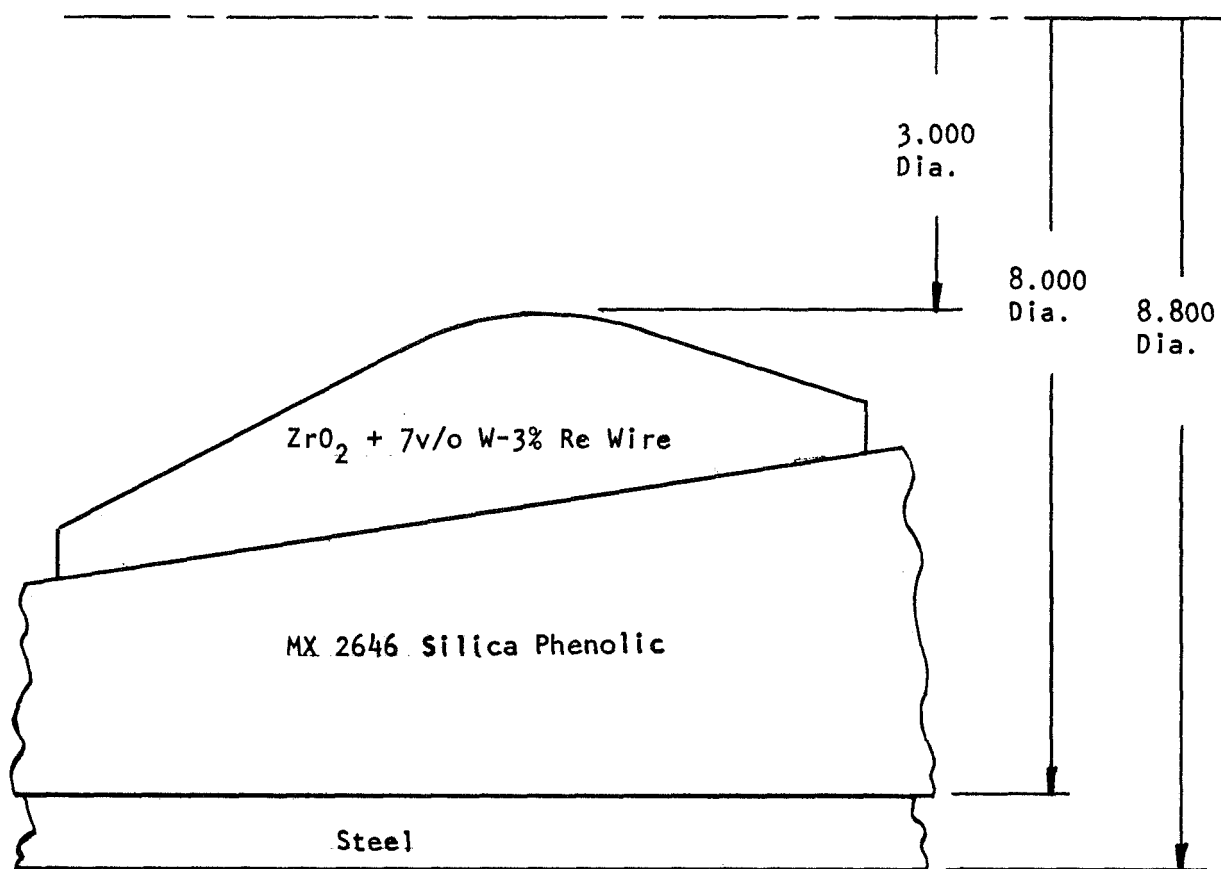


Figure 52. Nozzle throat assembly design used for thermal stress analysis.

TABLE 24

ZIRCONIA-TUNGSTEN COMPOSITE PHYSICAL PROPERTY DATA

Tensile Strength	70°F	2030 psi
	2000°F	2260 psi
	3000°F	510 psi
Compressive Strength	70°F	17,700 psi
	2200°F	24,000 psi
Density		6.3 g/cc
Poisson's Ratio	70°F	0.29
Thermal Conductivity	70°F	28.0 $\frac{\text{BTU-in}}{\text{hr-ft}^2-\text{°F}}$
	572°F	25.0
	1292°F	22.2
	1652°F	21.5
	2400°F	20.0
	5000°F	19.5
Specific Heat	70°F	0.1062 BTU/lb-°F
	2500°F	0.1537
	5000°F	0.1587

TABLE 25

SILICA AND STEEL PHYSICAL PROPERTY DATA

	<u>Molded Chopped Silica Phenolic</u>	<u>Steel</u>
Thermal Conductivity, BTU-in/hr-ft ² -°F	3.5	360.0
Specific Heat, BTU/lb-°F	0.24	0.10
Density, g/cc	1.78	7.58
Modulus of Elasticity, psi	0.9×10^6	29.0×10^6
Coefficient of Thermal Expansion, in/in/°F	2.6×10^{-6}	7.0×10^{-6}
Poisson's Ratio	0.2	0.3

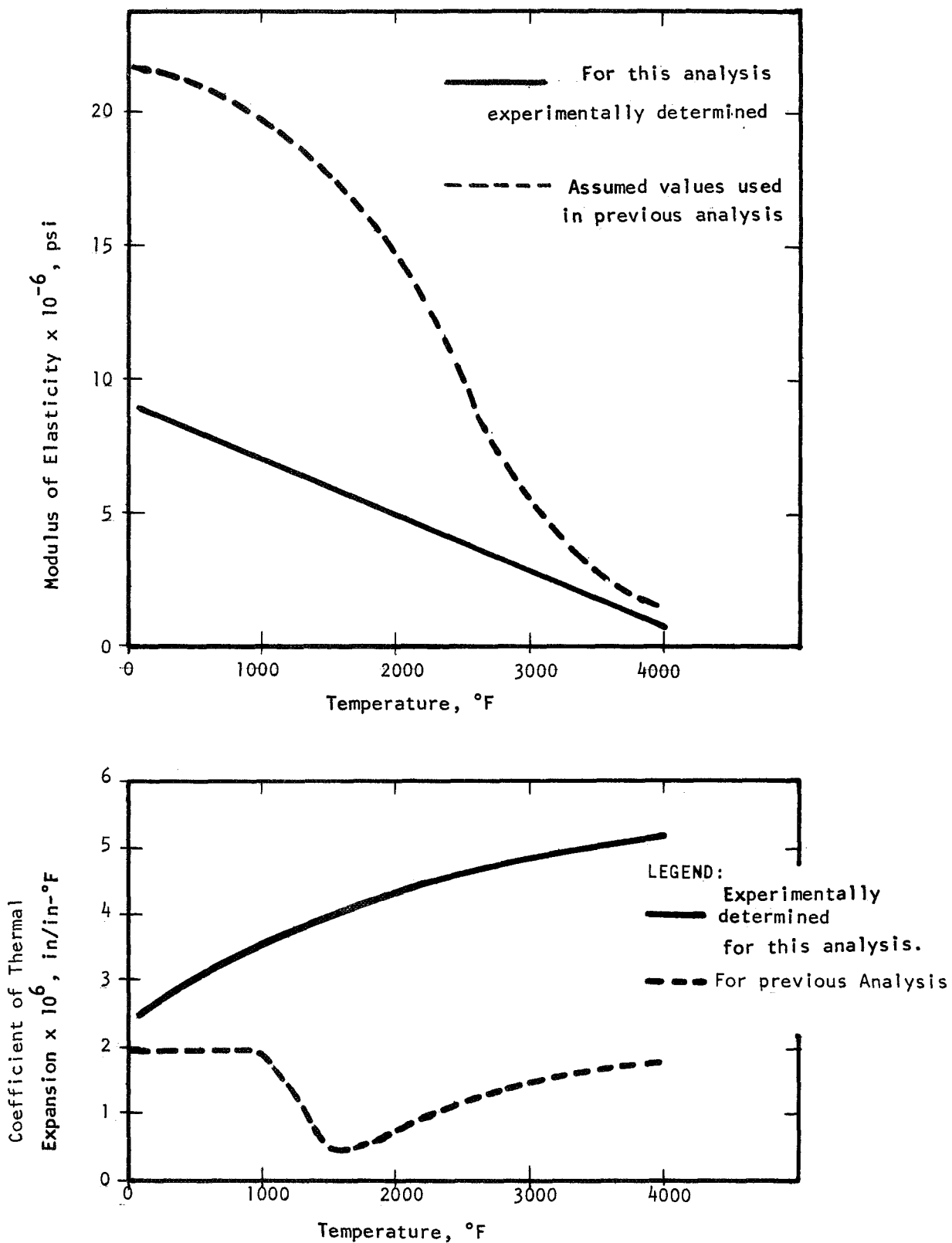


Figure 53. Modulus of Elasticity and Coefficient of Thermal Expansion for Zirconia - Tungsten Composites.

The results of the heat transfer analysis are presented in Figure 54. Predicted temperature gradients across the insert are shown at 8, 18, 100 and 300 seconds of elapsed firing time. As shown in Figure 54, the maximum temperature gradient across the throat insert of about 3920°F occurs at approximately 18 seconds of elapsed firing time.

Analysis of the support materials reveals all temperatures are within established operational limitations. The steel temperature is predicted to remain at ambient conditions for 300 seconds of elapsed firing time. For a 300-second test, the zirconia-to-silica-phenolic interface is predicted to rise to 1500°F which is below the melting temperature of silica (silica melts at approximately 3100°F). The silica phenolic material will be charred to a depth of approximately 0.080 inches at 300 seconds assuming a charring temperature of about 800°F. The zirconia-to-silica phenolic interface temperature is predicted to rise to 800°F at 197 seconds of elapsed firing time, thus some loss in support will occur due to charring.

By comparison to the preliminary analysis that was based on estimated property data, a significant reduction in the backside temperature of the ZrO_2 composite is predicted (1500°F as compared to 3000°F) resulting in lower char. The reason for this is that the thermal conductivity values used for this analysis (see Table 24) are approximately 40% as large as those estimated for the preliminary analysis.

Thermal stress analysis - Thermal stress analysis was conducted on the design presented in Figure 52. For the analysis, a TRW thermoelastic stress analysis computer program was used. This program, designated TRW Computer Program 80005, computes the combined thermal and pressure stresses in composite cylinders. For the thermoelastic stress analysis, it was assumed that the chamber pressure was 100 psia, thus the internal pressure at the throat surface was about 55 psia. Radial temperature distributions used in the stress analysis were those predicted by the heat transfer analysis.

The results of the stress analysis for a fully supported ZrO_2 composite throat are presented in Figure 55. Internal surface hoop and axial stresses are predicted to be in compression for 300 seconds of elapsed firing time. The maximum compressive stress of about 77,000 psia is a hoop stress and is predicted to occur at 1 second. The predicted compressive stress exceeds the compressive strength of the material (see Table 24), thus a failure of the inside surface material in compression is predicted. With the compressive failure of the material at the inside surface, the predicted stresses for the remainder of the test time as shown in Figure 55 are not realistic because of the reduced load transmitting capability of the material. Thus the hoop tensile load would be lower than that predicted (see Figure 55).

By comparison with the preliminary analysis, the predicted compressive stresses are high at the inside surface by a factor of 2 due primarily to the greater coefficient of thermal expansion (see Figure 53). The predicted external tensile stresses are lower (by a factor of 4) due to the lower thermal conductivity of the material when compared to the previous analysis

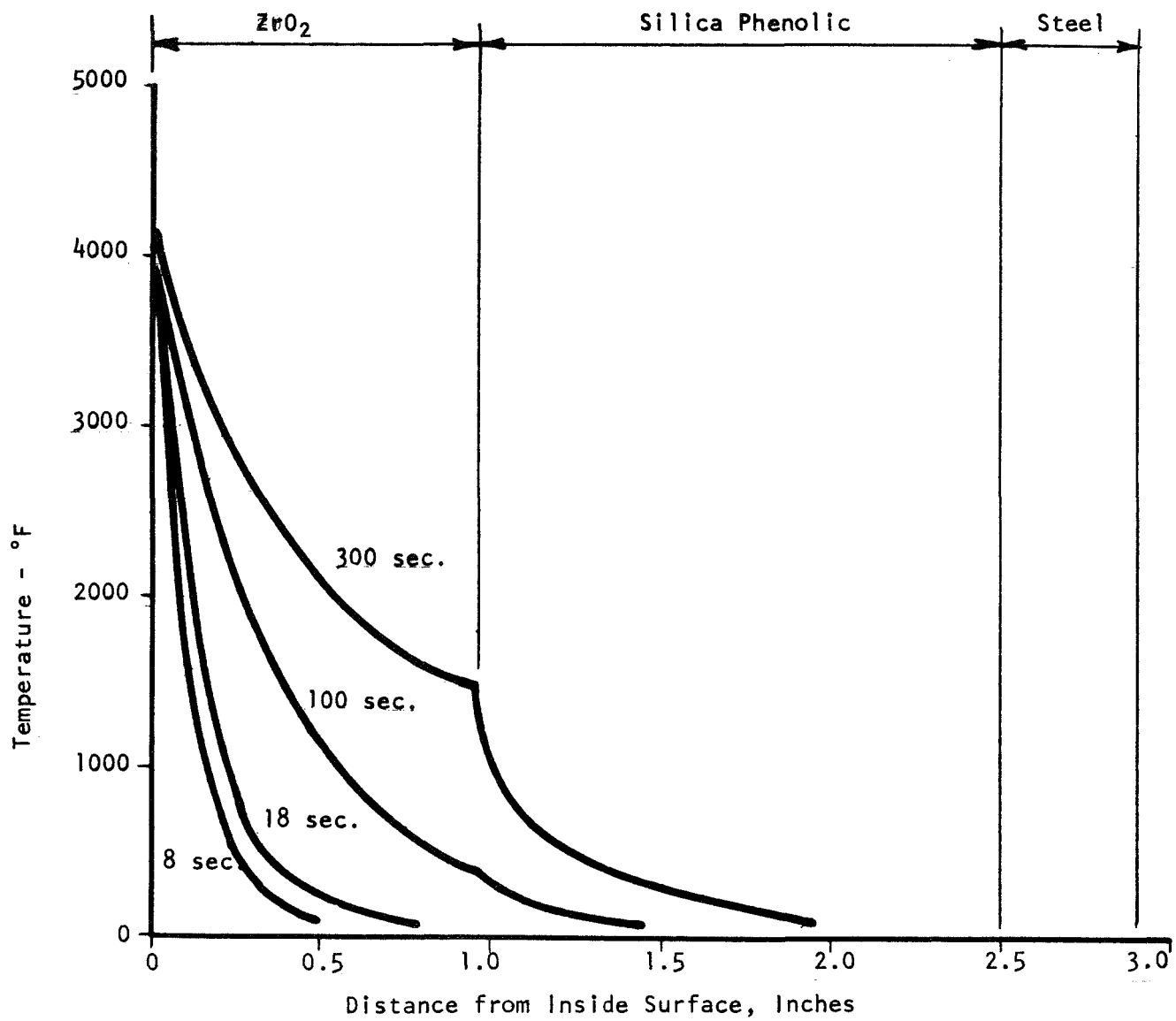


Figure 54. Predicted Temperature Profile

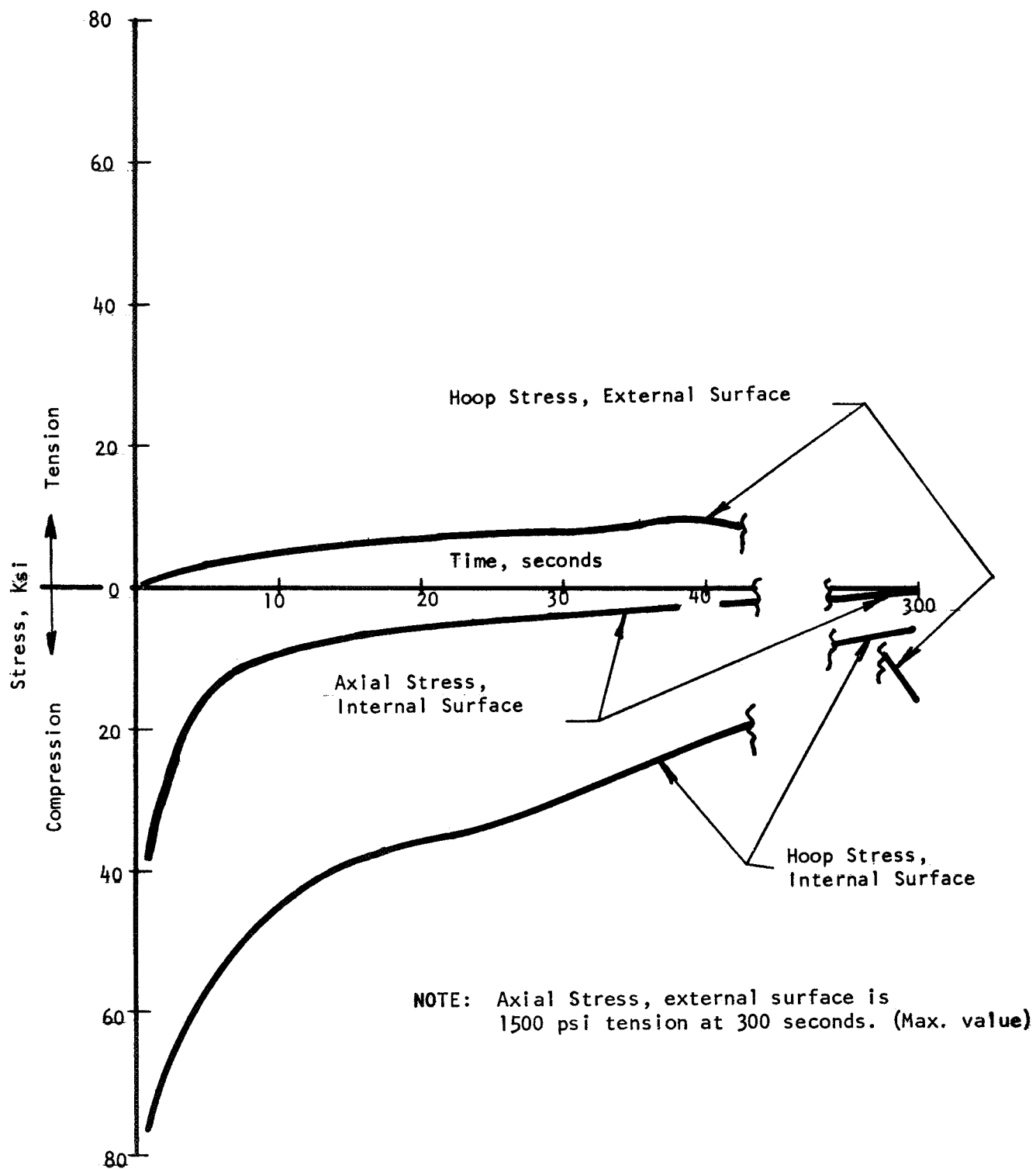


Figure 55. Predicted Stress for Fully Supported Zirconia-Tungsten Composite.

This results from the fact that a greater area of the ZrO_2 material near the external surface is put in tension thus reducing the unit tensile stresses in the material.

3. Insert Preparation

The insert was fabricated by isostatic pressing around a removable metal mandrel. The blended mixture of zirconia and chopped wire was sealed into a rubber mold around the metal mandrel and isopressed at room temperature at 30,000 psi pressure. The isopressed insert is pictured in Figure 56 prior to vacuum sintering.

The pressed insert was vacuum sintered for 4 hours at 4000°F. A heating rate of 250°F per hour was used with a cool-down rate of 500°F per hour. The sintered insert was machined to the configuration shown in Figure 51. The density of the machined insert was measured by water displacement as 6.3 g/cc which is about 94% of theoretical density.

A photograph of the completed insert is shown in Figure 57. As can be noted in Figure 57, there is a circumferential area on the O.D. of the insert near the exit end which did not contain enough material to fill the final contour during machining. This condition was probably caused by insufficient packing of the material in this area during the die loading. (The presence of the 7 v/o of fibers in this composite makes the packing of the powder into the isopress mold very difficult). As a result of discussions with NASA personnel, it was decided that this void could be filled by the zirconia-base slurry used as a potting material when the insert is built into the nozzle assembly. By this procedure, the insert would be suitable for test firing, and accordingly, it was delivered to NASA for that purpose.

4. Test Firing and Results

The test firing was carried out at NASA-Lewis Research Center, Cleveland, Ohio. A propellant combination of N_2O_4 /50% N_2H_4 -50%UDMH was used at a mixture ratio of 2.0. The test consisted of an initial 300-second firing, five 20-second pulses and a final 300-second test. The throat assembly was removed from the test engine after the initial 300-second test for visual examination and photography. The 20-second pulses were carried out with a 30 minute cooling period between pulses. The insert was examined visually on the test stand after each pulse.

No loss of performance was observed during any of the test cycles. A slight shrinkage of the throat, amounting to an 8% decrease in throat area occurred. The decrease in throat area was attributed to thermal expansivity and a volume increase due to the formation of microcracks within the composite.

After the completion of the final 300 second test, the insert was removed from the silica phenolic back-up support for examination. The insert had developed visible cracks in the matrix material on the O.D. surface, but no structural failure had occurred. The I.D. surface was pitted and rough, and some surface spalling had occurred, presumably because of deterioration of the reinforcing wires adjacent to the I.D. surface.



Figure 56. Isopressed billet of Type C material used in fabricating the 3 inch I.D. throat insert.



0 1 2 3

Figure 57. Machined Type C zirconia composite throat insert.

The insert was returned to the TRW Materials Laboratory for post-test analysis. This analysis is discussed later in this section of the report where the results are compared to those of the various other inserts tested during this program.

Concurrent with the testing of the insert of the Type C composite, an insert of Type A material, that had been supplied to NASA previously under a separate contract, was also subjected to the same test firing sequence. This Type A nozzle also successfully withstood the 700-second test firing sequence. However, the Type A composite proved to be less thermal shock resistant than the Type C material. This was evident by the formation of four axial cracks at about 90-degree intervals in the nozzle. In addition, a circumferential crack about midway in the length of the nozzle separated the nozzle into two washer type layers. Except for these cracks, however, very little deterioration occurred. There was no measurable throat erosion, and the exposed surface showed less spalling and generally better appearance than the Type C nozzle material.

As stated above, these nozzles showed no increase in throat diameter during test firing. In fact, a slight decrease in throat diameter was generally experienced during these tests. There are several mechanisms that could account for such a decrease in throat diameter. First, the temperature of the nozzle reaches a temperature in excess of its original sintering temperature, so further sintering of the nozzle may take place. Because of the relatively high density (90-95% of theoretical) of these nozzles and the fact that these highest temperatures are localized at the I.D. surface, this effect is expected to be minor. Another effect is that these high heat flux pulses tend to form microcracks within the composite. This, in effect, lowers the density of the material as it expands to accommodate this microcracking. Since the O.D. of the nozzle is restrained, this expansion of material volume results in a decrease in throat diameter. It is expected that this effect accounts for most of this throat reduction phenomenon.

The change in throat diameter for the various nozzles tested in this program are shown in Figure 58. The data for the Type C and Type A nozzles are shown here together with the data for other nozzles tested later in the program as discussed below.

B. Second Reinforced Insert

The purpose of this nozzle was to allow the incorporation of any changes in material and/or design that was indicated by the test firing results of the first nozzle. The generally successful test firing of the first nozzle indicated that only some minor material modifications should be considered.

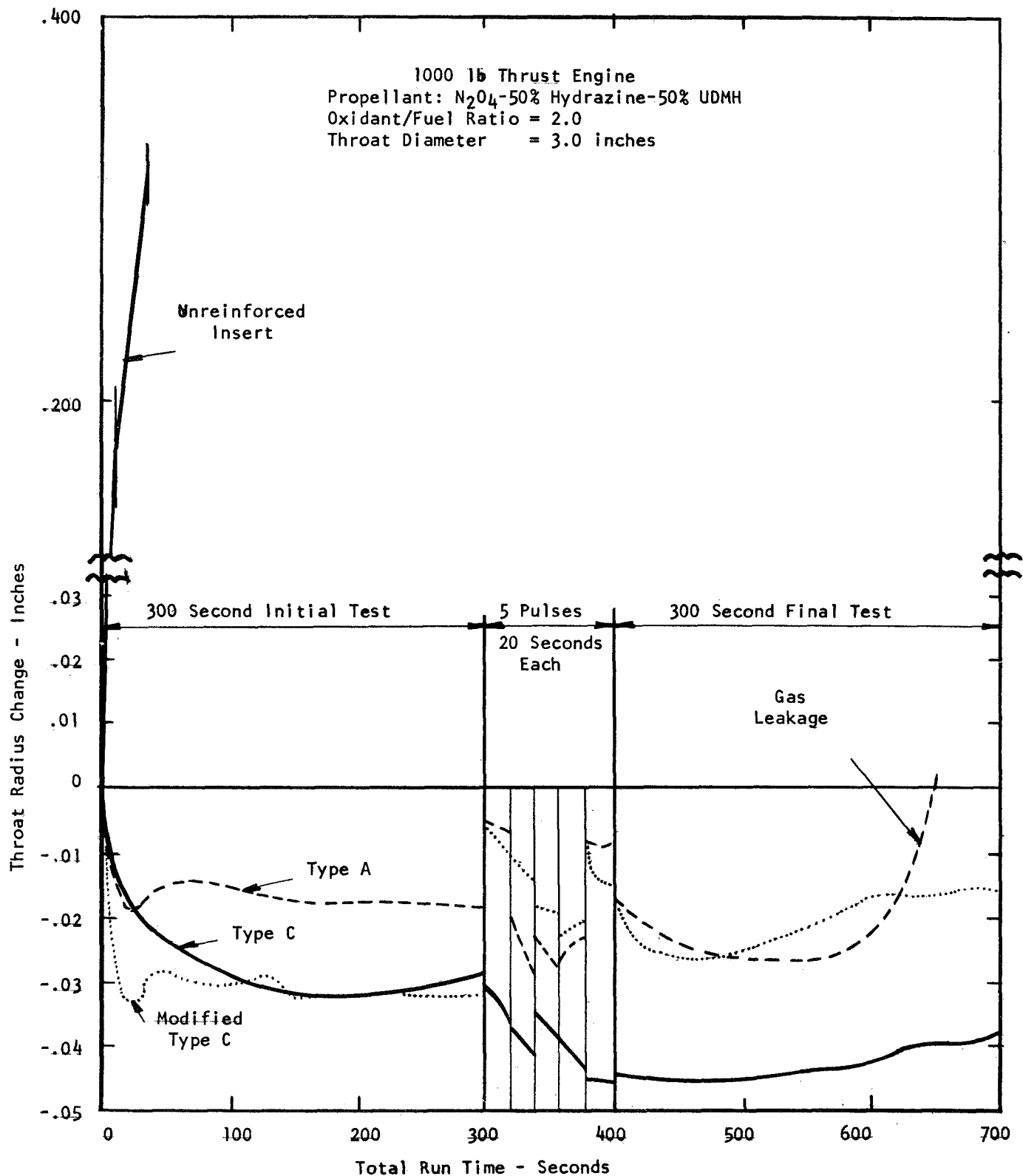


Figure 58. Change in throat diameter during rocket engine test firing for the nozzles tested during this program.

1. Material Selection

Based on the data generated during the earlier portions of the program and the performance of the Type C material during the test firing, a composite of the 2.85% MgO-stabilized zirconia reinforced with 7 v/o of 3.5 mil diameter x 3/16 inch long W-3%Re wire was selected for the second test insert. The choice was made to provide more oxidation protection at the I.D. surface by the use of a larger wire diameter. It was thought that this might improve the surface spalling characteristics of nozzles made from this material. The insert configuration and fabrication procedures were the same as were used in producing the first of the series of test inserts.

A photograph of the completed insert is shown in Figure 59. Density of the machined insert as measured by water displacement was 6.2 g/cc which is about 94% of theoretical density.

2. Test Firing Results

The test engine, firing conditions, and nozzle backup assembly were the same as were used for test firing the first insert in the series.

The test cycle used for the second insert consisted of a 300-second initial firing, five 20-second pulses and a 295-second final test firing. The final pulse was terminated at 295 seconds when the engine ran out of fuel.

A slight amount of throat erosion was noted during the final 295-second test as indicated by a slight increase in fuel flow. Measurements of the insert at the conclusion of the test disclosed a slight close-in amounting to a 0.016 inch reduction in the throat radius. The close-in of the throat was attributed to an increase in the volume of the insert due to microcrack formation as discussed above. For comparison, the first throat insert, which underwent no erosion during the test firing, had a throat radius close-in of 0.040 inches. This relationship is shown graphically in Figure 58.

This insert retained structural integrity after the firing sequence, so it was removed from its back-up structure in one piece for subsequent post-test analysis.

C. Unreinforced Zirconia Insert

In order to obtain a definitive demonstration of the important function of the reinforcing wires in a reinforced oxide, an unreinforced nozzle was produced of the same matrix material and by the same processing as the reinforced nozzle. This approach would not be expected to produce the best unreinforced nozzle available by current ceramic technology, but it would serve as a valid empirical demonstration of any improvement afforded to a ceramic structure by the reinforcing wires.

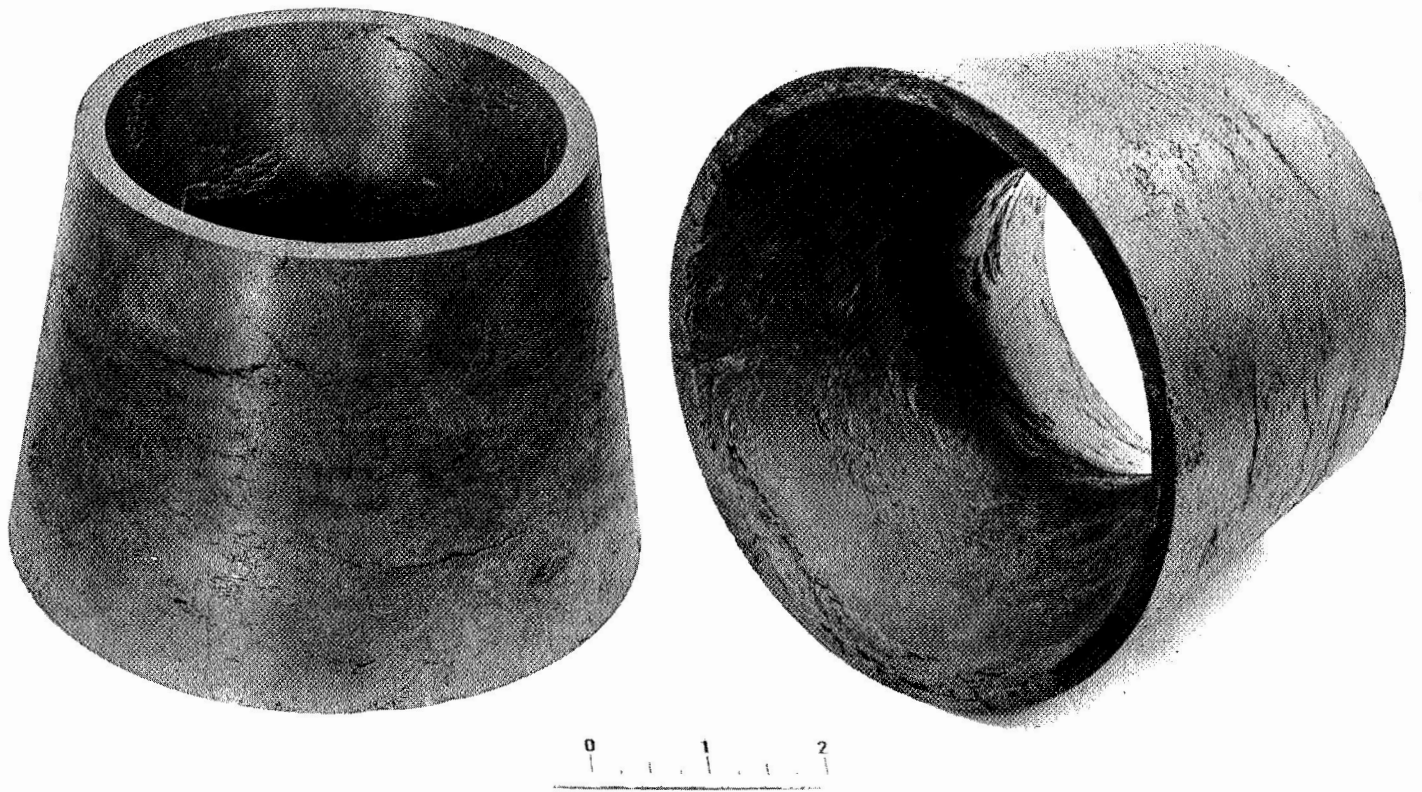


Figure 59. Second zirconia composite throat insert Type C (modified)
3.5 mil wire 7 v/o.

1. Insert Preparation

The third insert was fabricated with the same unreinforced zirconia matrix material that was used in the first two test inserts. The sintering of crack-free compacts of unreinforced zirconia however, proved difficult. The processing parameters used to fabricate reinforced composite structures were not applicable to the fabrication of relatively massive unreinforced structures.

The use of the fine particle size ZrO_2 powder, needed to insure good bonding in the composite materials, resulted in shrinkage cracks when unreinforced compacts were sintered with the same cycles as were used for fabricating composite materials. The pressed insert was sintered at a heat-up rate of $250^\circ F/hr$ (used for composite materials) and cracked severely. Another pressing was then sintered using a heat-up rate of $167^\circ F/hr$. This insert, shown in Figure 61, also cracked, indicating that extending the heat-up cycles alone would not eliminate the problem. Accordingly, a powder blend containing a mixture of fine and coarse particles was selected to minimize sintering shrinkage. The material from the first as-sintered nozzle was crushed to yield a coarse grout which was blended with the finer as-received zirconia powder as follows:

- 30% Crushed grout from scrap nozzle - (-40 +325 mesh)
- 45% 2.85% MgO-stabilized ZrO_2 - Fine Texture
- 25% 2.85% MgO-stabilized ZrO_2 - Medium Texture

This material was isopressed and then vacuum-sintered. The normal 4-hour vacuum sintering treatment was used except that the heat-up and cool-down rate were reduced to $60^\circ F/hr$. The nozzle therefore, required a 66-hour program to reach temperature and another 66 hours to cool down before removal from the furnace.

The as-sintered nozzle was sound (in one piece with no cracks). However, extreme residual stresses in the part were evidenced by spontaneous O.D. surface spalling and edge cracking occurring after the nozzle was removed from the sintering furnace. None of the surface spalling or cracking was deep enough to affect the as-machined dimensions. During machining, a longitudinal crack running the length of the nozzle developed. However, since the insert was still in one piece, the machining was completed and the insert delivered to NASA for test firing. The machined insert is shown in Figure 61. The density of the finished nozzle was 5.4 g/cc which is about 92% of theoretical. There was no measurable open porosity in the nozzle.



Figure 60. As-sintered unreinforced zirconia insert showing effects of the 167°F/hr heating rate during the sintering cycle.

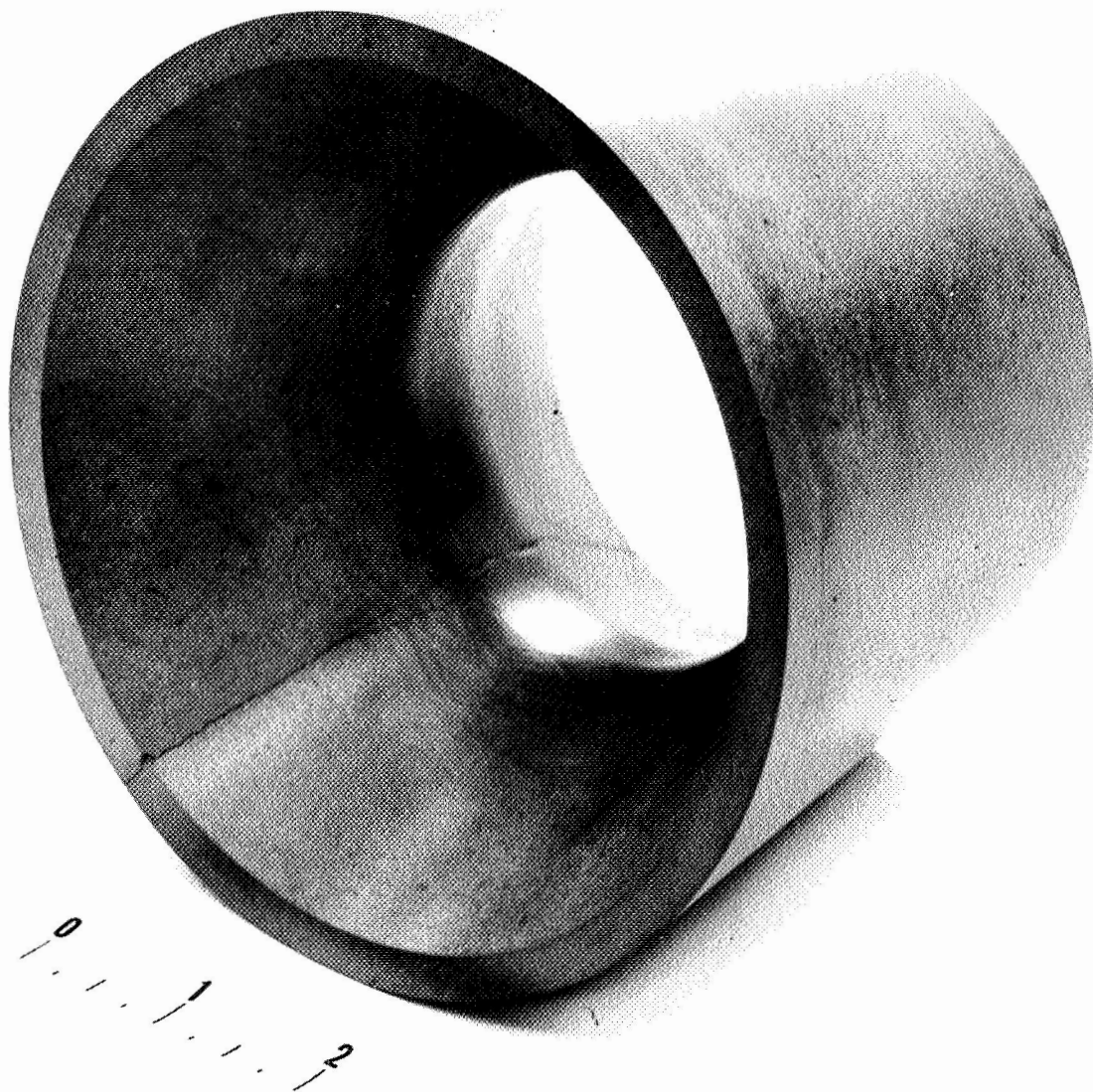


Figure 61. Unreinforced nozzle made from 2.85% MgO stabilized zirconia powder.

2. Test Firing and Results

The firing test was conducted under the same conditions as the preceding two inserts tested in this program.

The initial test firing was aborted after 6.7 seconds because of increased propellant requirements to maintain a constant chamber pressure which indicated an increase in throat area to approximately 25%. Examination of the insert after the test revealed an increase of the throat radius of 0.182 inches.

Because the insert was still structurally sound it was decided to refire it. The second firing was stopped after 15 seconds because of excessive propellant requirement indicating excessive throat erosion. Erosion of the throat during both test firings was continuous. The throat radius had eroded 0.327 inches after the second test and the insert had developed numerous cracks extending through the walls. The presence of the original longitudinal crack, which occurred during machining of the insert, had apparently played no part in the failure of the insert.

The mechanism of erosion appears to be a fracture of granules of zirconia at the hot face due to surface thermal shock cracking. The loose granules are then swept away by the gas stream. Mechanical erosion alone appears to have little, if any, effect on the erosion rate.

D. Post Test Analysis of Nozzle Inserts

Both the first (Type C) and second (modified Type C) throat inserts were examined after their respective test firing cycles to determine their degree and type of degradation. This examination consisted of visual, metallographic, and electron microprobe analyses of the nozzles.

1. Visual Examination

The main feature of both nozzles was that some reaction of the exposed surface had taken place. This resulted in a roughening and some spalling of the surface. This effect was more apparent on the modified Type C insert than on the first Type C insert. Neither of the inserts showed any evidence of reactions between the back-up materials and the insert material, although both inserts were darker in color after the test firing due to a slight amount of carbon pickup from the supporting structures. Views showing the inside surface of these nozzles are shown in Figures 62 and 63.

Aside from this surface spalling, the other main type of degradation apparent by visual examination was an irregular pattern of microcracking observed on the O.D. of the insert. The cracks in the first (Type C) insert were slightly more numerous and smaller than those observed on the second (modified Type C) insert. Views illustrating this are shown in Figures 64 and 65.

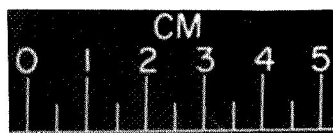
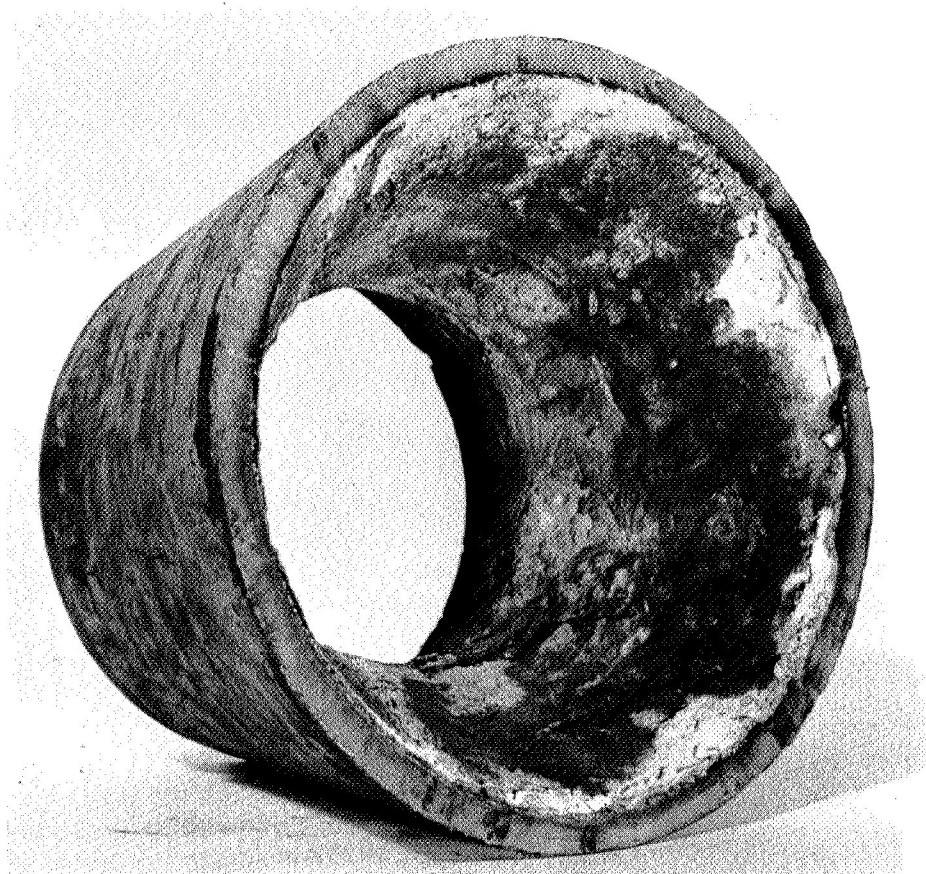


Figure 62. Type C (7 v/o of 2.0 mil wire) zirconia composite throat insert after 700-second test firing.

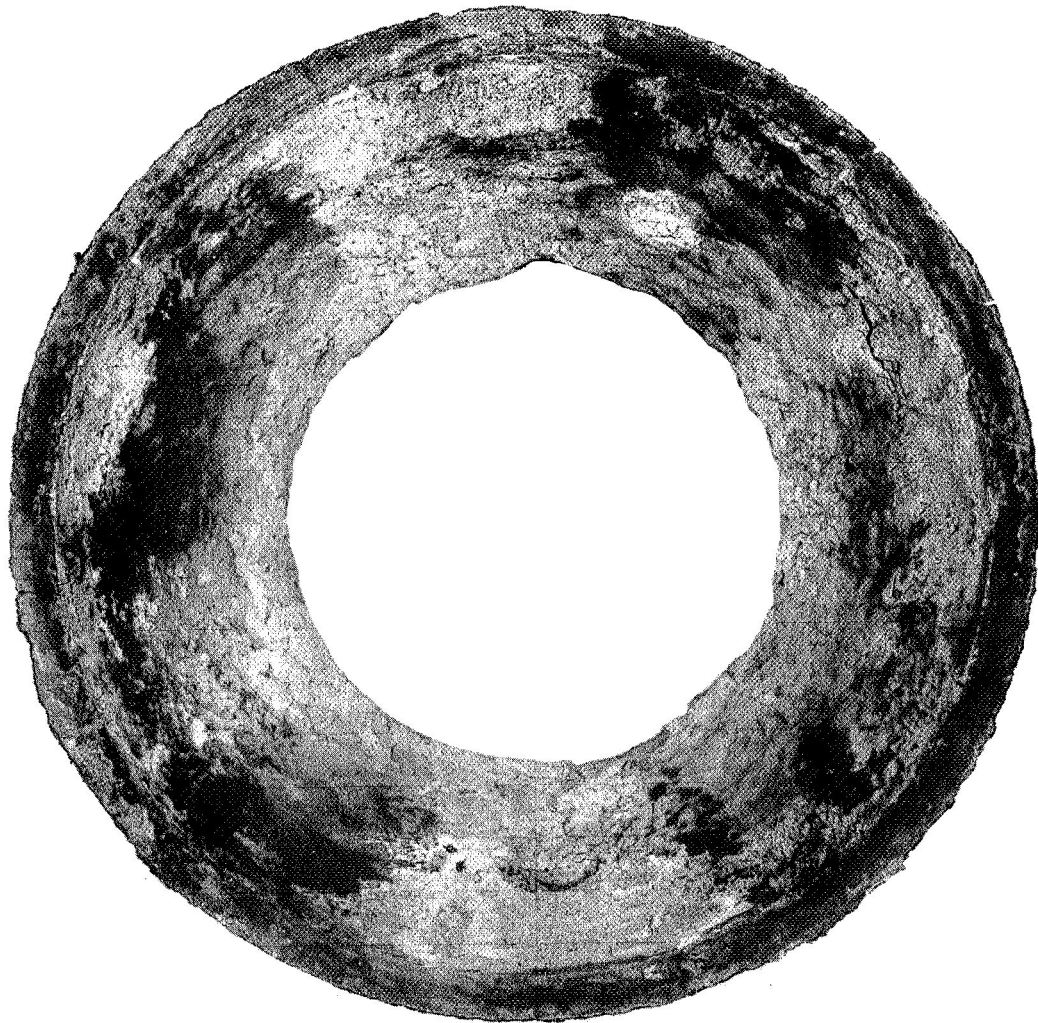


Figure 63. Type C modified. (7 v/o of 3.5 mil wire) zirconia composite throat insert after 700-second test firing.

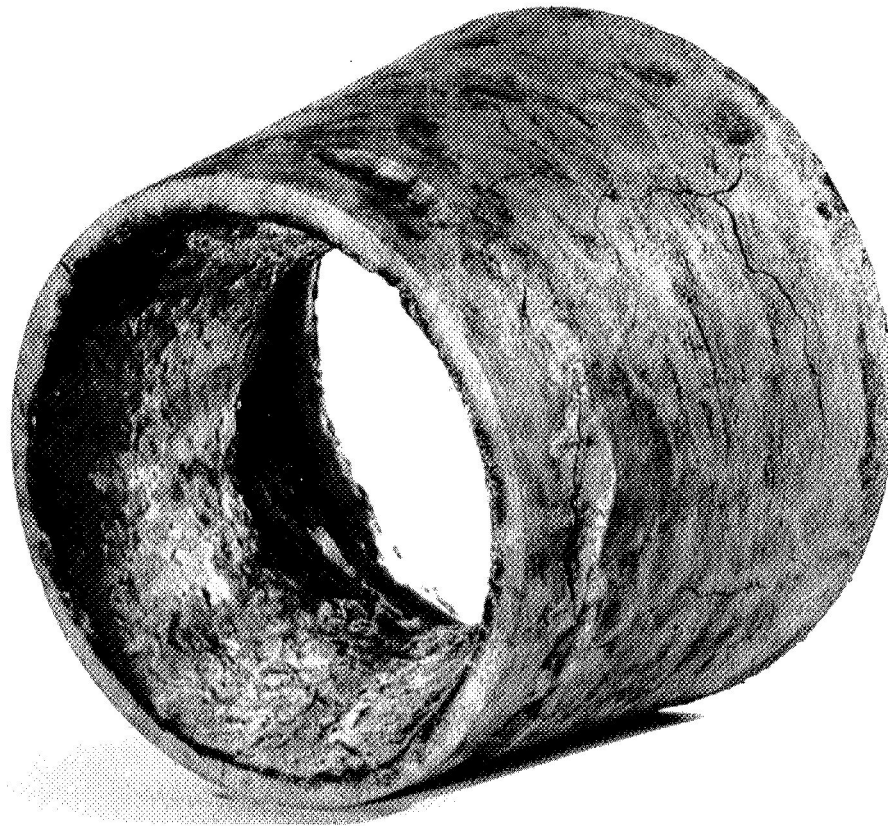


Figure 64. Type C (7 v/o of 2.0 mil wire) zirconia composite throat insert after 700 second test firing.



Figure 65. Type C modified (7 v/o of 3.5 mil wire) zirconia composite throat insert after 700 second test firing.

Visual examination of the cross-section of these nozzles (Figures 66 and 67) show the existence of these microcracks. Some indication concerning the depth of material deterioration from the I.D. surface can also be gleaned from such an examination.

The test firing of the Type C material containing 7 v/o of 2 mil diameter wire resulted in a final net throat radius reduction of 0.040 inch compared to 0.016 inch for the second insert which contained the 3.5 mil diameter wire. This indicates that the 2.0 mil wire offered more erosion protection than the 3.5 mil wire reinforcement. This agrees with the observation that the I.D. surface of the 2.0 mil composite was less roughened by the 700 second test firing than the I.D. surface of the 3.5 mil composite.

2. Metallographic Examination

Another measure of material degradation during test firing was obtained by metallography.

Typical microstructures of these materials after test firing are shown in Figures 68 and 69. Figure 68 shows a cross section of the hot face at the throat centerline. The hot face has a spongy appearing zone approximately 5 mils thick. The spongy effect is due to diffusion of the tungsten 3% rhenium wire into the zirconia and subsequent removal by oxidation. The composite structure immediately behind this layer appears unaffected except for the presence of microcracks and a slight recrystallization of the tungsten alloy wire. The microstructure of the interior of the composite shown in Figure 69, is also unaffected except for the microcracks between the supporting wires.

3. Microprobe Analysis

Microprobe analysis was performed by the same techniques used previously on the oxidation tested composite specimens. As before, the presence of tungsten was measured as a function of the distance from the exposed surface of the specimen. The data were more difficult to interpret in these nozzles because of the surface spalling and microcracks present in the structure. Nonetheless, the general behavior was the same as that shown in the microprobe trace obtained on the oxidation specimen (Figure 44). That is, the surface was depleted in tungsten; an intermediate zone showed an intermediate level of tungsten diffused throughout the zirconia; and an unaffected zone was present with the expected intermittent tungsten signal corresponding to the fiber locations. This information supports the character of the composites that is evident by metallographic analysis.

4. Summary of Nozzle Evaluation

From the general depth of deterioration found in these nozzles coupled with the fact that throat shrinkage rather than throat erosion occurred, it appears that these nozzles could have successfully withstood even longer firing times. It is expected that the microcracking would eventually lead to further spalling by fiber loss due to oxidation.

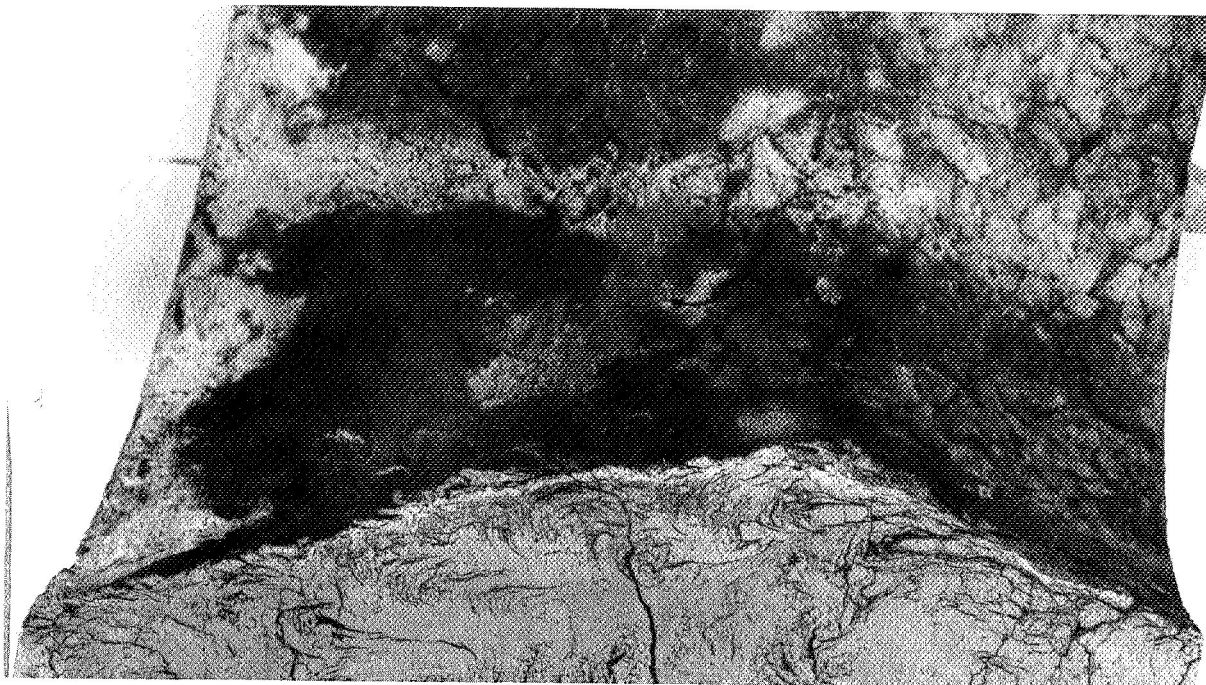


Figure 66. Cross section of zirconia composite throat insert Type C material, (7 v/o of 2.0 mil wire) after 700 second test firing.

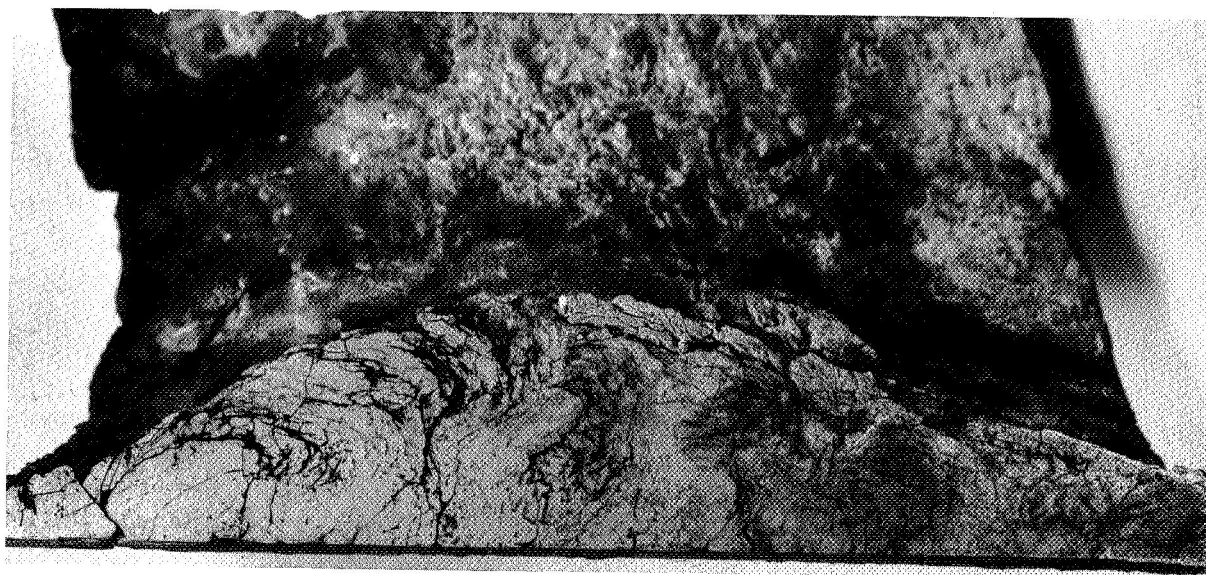
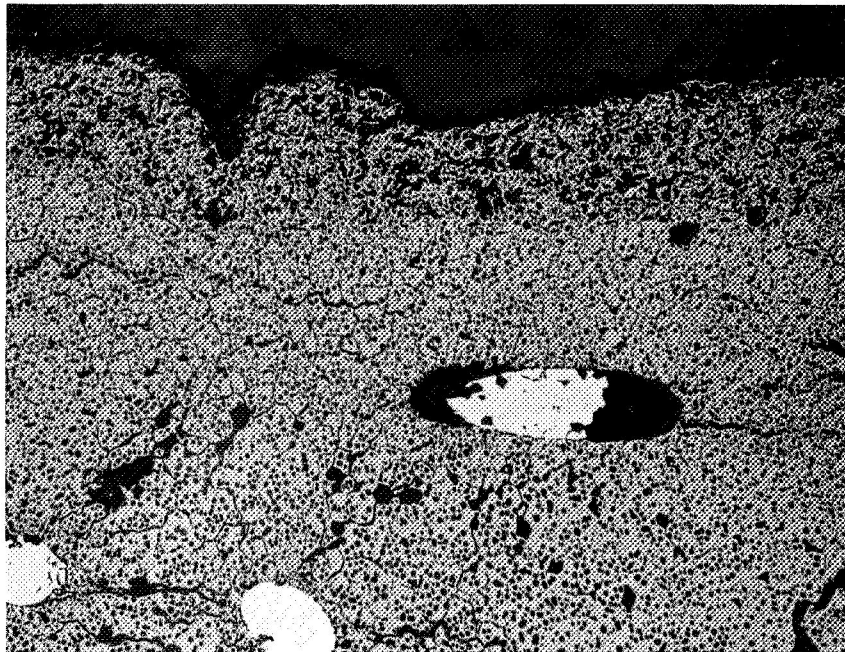
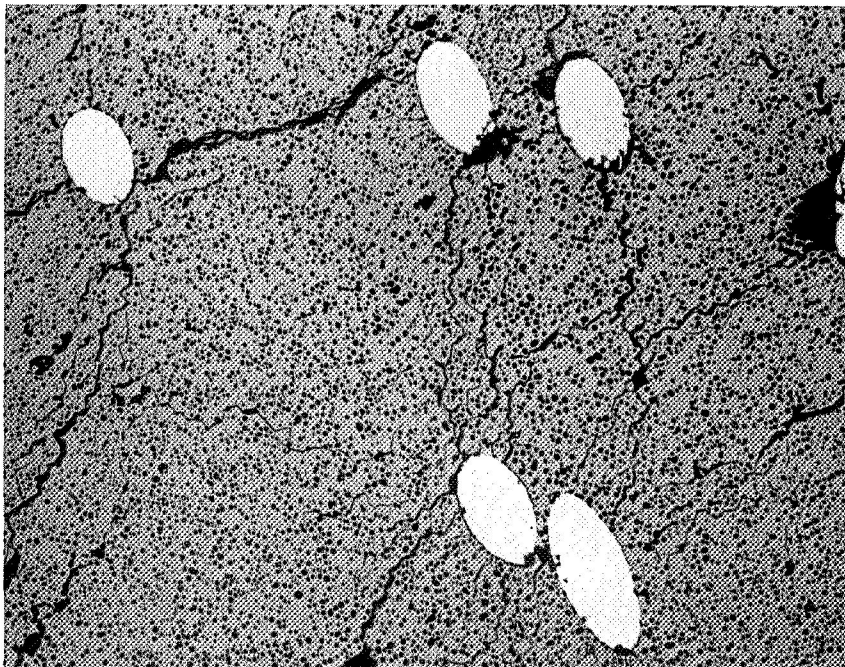


Figure 67. Cross section of zirconia composite throat insert Type C modified (7 v/o of 3.5 mil wire), after 700-second test firing.



100X

Figure 68. Throat cross-section of post fired insert, Type C modified composite material.



100X

Figure 69. Interior section of post fired insert, Type C modified composite material.

This would finally result in throat erosion. The parabolic oxidation rate indicated in the propellant oxidation tests indicated that such degradation, however, might take increasing amounts of time for equal increments of deterioration to occur.

The modified Type C material contained 3.5 mil wires rather than the 2-mil wires of the initial Type C insert. This change was made to retard the effects of fiber oxidation by virtue of the thicker wires. Making this change while keeping the same volume percentage of wires, results in about a five-fold decrease in the number of wires in the composite. The resulting reduction in the homogeneity of the composite apparently outweighs any improvement in the fiber oxidation behavior. The original Type C material with the 2-mil wire remained the most promising composite studied in this program based on the combined criteria of resistance to cracking, surface characteristics, and erosion resistance. This material offers the best starting point for developing any further modifications that may be required for other specific applications.

CONCLUDING REMARKS

This final section of the report will comment on the results of the program from an overall perspective. These comments will serve as a basis for discussing some of the future possibilities of exploiting the technology developed in this program.

A. General Program Results

As a frame of reference, the objective of the program was to obtain an understanding of the variables associated with wire-reinforced zirconia throat inserts and, thereby, develop improved throat inserts of this composite material in a larger size than previously demonstrated. This dual objective of obtaining both basic knowledge and improved hardware was met in this program. The test firing results described in this report demonstrated the improvements obtained in nozzle insert performance. The battery of tests and evaluation techniques used throughout the study allowed a systematic approach to the optimization of this type of composite material.

From all overall evaluation, the Type C composite was shown to be the best material studied for this application. At the start of the program, an F410 matrix material using 5 v/o of 3.5 mil diameter wire could be considered the state-of-the-art. This program, therefore, identified a different matrix material (2.85% MgO-stabilized zirconia) a different wire diameter (2-mils), and a different wire content (7 v/o) as the constituents of the optimum Type C composite.

It may seem surprising that even a greater departure from past practice was not indicated in this program. It is noted, for instance, that the prior "state-of-the-art" material is nominally the Type A composite, which can be considered the "runner-up" composite in this program. It is further noted that the reinforcing wire alloy used prior to this program also was shown in this program to be the best available for this application. Based on such considerations, it may seem that a lot of effort was expended in this program to develop what may appear to be only minor changes and improvements in this material. One answer to this assessment is that these past efforts, although based on sound metallurgical and ceramic technology, were indeed fortunate to come as close as they did to an optimized material with the limited experimental effort that was associated with them.

In addition to hardware improvement, a major contribution of the present program was the definition of some of the basic factors pertinent to the development of an effective reinforced ceramic. As a result of this facet of the program, the behavior of the Type C composite, for example, is predictable. Furthermore, it is known what general effects variations in wire content, size, etc. will have on the properties of the composite. Therefore, some firm guidelines are available for use in further development of this type of material.

An example of this is the Type A composite which, as noted above, is the same nominal composition as used prior to this program. Considerable difficulty, however, had been encountered in fabricating this material in the past because of particle size variations existing between various lots of the same nominal F410 zirconia powder. This factor was recognized in this program, and the F410 particle size was properly controlled so that desirable, reproducible results were obtained with the Type A composite. In this regard, the Type A composite, although nominally equivalent to prior material, actually represents an improved composite resulting from this program. Equally important is the fact that this zirconia matrix material can be specified in the future and can be expected to result in the desired composite properties.

Some comments are in order concerning the Type C composite material. First of all, it is interesting to note that the matrix material (2.85% MgO-stabilized, fine-texture zirconia) was not one of the most promising materials based on thermal shock behavior of the unreinforced samples (refer to Table 13). The medium-texture sample of this same composition did, however, show good thermal shock properties; it consequently became a constituent of the Type B composite. In evaluating these composites containing the medium-texture zirconia, it appeared that a finer particle size of zirconia would be desirable to give increased density in the composite. The fine-textured zirconia of this same composition was, therefore, reinstated into the program as a constituent of a reinforced composite. The finer wire proved more compatible with this finer zirconia. The finer wire also was more adaptable to higher wire contents, so the final Type C composite contained 7 v/o of the 2-mil wires. The medium-texture composition was used with 5 v/o of 3.5 mil wire (Type B composite) but was shown to be inferior to the Type C composite by the rocket engine exhaust oxidation tests. The Type C composite was, therefore, chosen as the material to be used for the throat insert fabrication.

Changing the reinforcing wire diameter in the fine-textured zirconia from 2-mil to 3.5-mil to form a "modified Type C" composite also resulted in a sound composite structure. However, the second throat insert, which incorporated this modification, showed no improvement in test firing behavior. In fact, slightly increased spalling of the exposed surface was encountered. Therefore, the unmodified Type C composite remains the best overall material for this application.

The indispensable role of the fibers in imparting durability to the composite was dramatically illustrated by the test firing results of the unreinforced nozzle. Whereas the reinforced nozzles withstood a 700-second accumulation of rocket firing with no measureable throat erosion, the unreinforced nozzle experienced a 25% throat area increase in just 7 seconds of test firing. This helps demonstrate the promise that fiber reinforcement holds in extending the use of ceramics for both rocket nozzles and other applications where ceramics are desirable except for their brittleness and thermal shock limitations.

B. Possible Future Applications

The above discussion shows that this program has developed a promising rocket nozzle insert material. Some comments will be made here regarding how this type of material may find some specific applications.

First of all, this program has shown that the Type C composite can be made into satisfactory nozzles up to at least 3 inches in throat diameter for application in the N_2O_4 -hydrazine type of propellant systems operating at 100 psia chamber pressure. For multi-pulse applications not exceeding 700 seconds of firing time, this material concept can be used with confidence.

Extended usage should also be considered. This extension may take place in one of the following ways:

1. Extended number of cycles or firing time
2. Increase in nozzle size
3. Increase of severity of firing conditions.

1. Extended Firing Times

Under the test conditions used in this program, there was no net increase in throat area for these reinforced nozzles. The degree of material degradation and indicated mechanisms of attack would suggest that these nozzles retained a significant proportion of their useful life after the 700 second firing sequence. This would be true both with respect to longer periods of sustained firing and with respect to additional firing pulses. If such a longer-time application exists, this type of nozzle insert should be tested under these extended conditions to assess just what is their life expectancy before significant loss of engine performance is encountered.

2. Larger Throat Sizes

As the size of throat inserts increase, severe problems are faced both with respect to fabrication difficulties of large ceramic structures and also in regard to the increased severity of thermal gradients and resultant stresses associated with the use of more massive nozzle throats. This program was successful in scaling up this type of composite from 1-inch throat to 3-inch throats. Just how much additional scaling up is feasible can be finally determined only by a suitable experimental program logically associated with some specific application.

As this report is being written, one such application is being explored within TRW. This is the nozzle of the Lunar Module Descent Engine (LMDE). This nozzle design will require a throat of about 7 inches diameter, which, in turn, requires a ceramic structure of about 12 inches in overall dimension. This will indeed be a significant step forward if a one-piece nozzle insert can be successfully applied to this application.

One possible way of building larger inserts from this material is to use a segmented design, a layered design, or a combination of these concepts. This may facilitate both the fabrication and performance limitations that may otherwise be faced in such massive ceramic parts. For example, the Type A nozzle, produced under separate contract but discussed above in regard to its comparative performance, formed axial cracks at about 90 degrees around the insert. In addition, a circumferential crack was formed which effectively separated the nozzle into two washer-type layers. This behavior would indicate that if a segmented - layered design had been used, each constituent segment would not encounter a severe enough thermal stress to form further cracking. This specific approach is, in fact, being pursued under current NASA contract which specifies a 3-inch throat insert of Type A composite (chosen for its good surface characteristics and freedom from spalling) to be made in 3 washer-type layers each divided into 4 radial segments (for a 12-piece nozzle). This would should help demonstrate the feasibility of this approach for other larger-size nozzle throat designs.

3. More Severe Firing Conditions

This one additional avenue of extended application for reinforced oxide nozzles involves the operation of rocket engines under more severe (and correspondingly more efficient) conditions by variation either of chamber pressure, oxidant-fuel ratio, or type of propellant system. Zirconia melts in the 4700°F temperature range, so the increased throat temperatures resulting from more severe operating conditions may provide a limitation to the application of this type of insert. It is possible that other oxides, such as thoria which melts at over 5900°F, can be adopted to this reinforcing scheme to provide an extended range of application for this type of reinforced oxide throat insert.

At present, the upper limit of usefulness for zirconia still must be determined. Again, there is an approach underway within TRW which will help do this. A nozzle insert of the Type C material is currently being fabricated for evaluation by TRW Systems on an Air Force Program. (Contract F04611-68-C-0054) which will involve the same propellant system studied in this program except at an increase in chamber pressure from 100 psia to 300 psia. The results of this test firing will help give a more definite evaluation concerning the promise of reinforced zirconia throat inserts for these upgraded rocket engine applications.

As a final comment on this program, it is evident that an effective basis has been formed for the application of reinforced oxide throat inserts in rocket engines. A continued effort must now be carried out to make this technology known to those involved in rocket engine technology so that a full exploitation of this promising concept can be achieved.

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