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CERAMIC FABRICATION R&D

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EXECUTIVE SUMMARY

This project is separated into three tasks. The first task is a design and modeling effort to be carried out by MSE, Inc. The purpose of this task is to develop and analyze designs for various cohesive ceramic fabrication (CCF) components, including an MHD electrode for strategic defense initiative (SDI) applications and a high stress, low cost, reinforced ceramic component for armor applications. The MHD electrode design is substantially completed. A layered structure composed of molybdenum disilicide graded with quartz glass has been designed and analyzed using finite element methods. The design demonstrates the fabrication capabilities of the CCF process. The high stress, armor application component will be silicon carbide reinforced alumina in thick plates.

Task 2 is directed at establishing a mechanical properties data base for monolithic and laminated alumina fabricated using the CCF process. It has been shown that monolithic CCF alumina has properties equal to comparable commercial alumina in room and elevated temperature tests. Work on establishing similar data for bonded specimens of CCF alumina is continuing.

Task 3, subcontracted to Ceramics Binder Systems, Inc., involved production of a solid oxide fuel cell model electrode; however, work ceased when it became apparent that successful integration of the electrode modules would require additional time. Currently, work is focused on CCF processing of molybdenum disilicide for the model MHD electrode. It has been demonstrated that the CCF process can be successfully adapted to such a nonoxide material.

In parallel, the production of thick alumina plates using CCF processing is being pursued so ballistic test plates can be made. Reinforcement by incorporating silicon carbide platelets is being addressed. Consequently, the development of sintering aids to yield high pressureless sintered densities is being investigated.

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1.0 INTRODUCTION

The general goal of the cohesive ceramic fabrication (CCF) research and development project is to develop the CCF process and demonstrate its application to various defense-related systems.

The project has been separated into three individual tasks:

- Task 1 -- Ceramic Component Design and Analysis;
- Task 2 -- Exploratory Development Using the CCF Process; and
- Task 3 -- Ceramic Fabrication and Manufacturing.

2.0 PROJECT DESCRIPTION

2.1 TASK 1 -- CERAMIC COMPONENT DESIGN AND ANALYSIS

The purpose of this task is to develop realistic specifications for various CCF components that will demonstrate the applicability of the CCF process to defense systems, including a magnetohydrodynamic (MHD) electrode for strategic defense initiative (SDI) applications and a high stress, low cost, reinforced ceramic matrix composite with armor applications.

This task is the principal responsibility of MSE, Inc.

2.1.1 Subtask 1A -- MHD Electrode Design and Analysis

The overall thrust of this task is to design a ceramic MHD electrode having advanced characteristics using the unique capabilities of the CCF process. The initial design will be generated based on input from MHD and materials specialists and design requirements related to SDI applications. The design will then be analyzed using the finite element technique. It is expected that this will be an iterative process involving material changes and dimensional variations. The end product of this effort will be an electrode design used as the basis for fabricating the electrode in Task 3.

2.1.2 Subtask 1B -- High Stress Component Design and Analysis

In this subtask, a high stress ceramic component will be designed and analyzed. An armor application has been chosen from several possible components. The design calls for ballistic test plates and a curved shape. Only simple analysis and modeling is anticipated to be feasible.

2.1.3 Subtask 1C -- Project Management

This subtask entails managerial and technical supervision of Task 1 and Task 2 work. Technical monitoring and general oversight is carried out on Task 3, which is subcontracted to Ceramic Binder Systems (CBSi).

Effective May 1, 1990, Applied Technology Laboratories (ATL) merged with MSE, Inc., with no changes in personnel or location of facilities. Ron Glovan, Senior Materials Engineer for MSE, was appointed project manager.

2.2 TASK 2 -- EXPLORATORY DEVELOPMENT USING THE CCF PROCESS

This task deals with the generation of a scientific data base for ceramic materials produced using the CCF process. Emphasis is on alumina, but some nonoxide data on molybdenum disilicide will be generated. Data will be obtained to characterize the properties of monolithic and bonded (laminated) ceramic shapes.

2.2.1 Subtask 2A -- Characterization of Starting Materials

Only limited characterization of the starting materials was scheduled because manufacturer's specifications and data are sufficient for most purposes. Some chemical analyses and microstructural analyses were scheduled.

2.2.1.1 Subtask 2A-1 -- Ceramic Process Control Studies

Work previously conducted showed that aspects of the CCF process were inadequately understood and not reproducibly controlled. Therefore, a series of matrix experiments was designed to identify the causes of process-related defects encountered when thicker parts were attempted. The results are presented in this report. Meanwhile, successful production of MIL-STD-1942 test bars was achieved during the last reporting period.

2.2.1.2 Subtask 2A-2 -- Characterization of Sintered Ceramic

Sintered ceramic produced by the CCF process is evaluated based on the sintered modulus and modulus of rupture (flexure strength in four-point bending) and on an examination of the microstructure of the sintered material. A thorough examination includes average grain size, grain-size distribution, grain shape, and grain-shape distribution. Defect distributions are also significant, including crack lengths, widths, and distributions and void (pore) sizes, shapes, and distributions.

Grain size is important because strength is usually inversely proportional to the square root of the grain diameter. Hence, a fine, uniform grain size results in

high strength, but high strength also requires minimization of porosity, since pores and voids act as stress concentrators, which may substantially reduce strength.

Characterization of sintered microstructure for this project relies primarily upon scanning electron microscopy examination because of the fine grain size and small pore size in sintered ceramic.

2.2.2 Subtask 2B -- Mechanical Test Methods

Mechanical testing is necessary to secure quantitative information on the strength of ceramics produced by the CCF process. Monolithic ceramic will be tested to provide data for comparison with regular commercial ceramic and also to establish a baseline against which the strength of laminated (bonded) parts can be assessed. Testing to MIL-STD-1942 for flexure strength is planned in addition to other testing conducted to ascertain fracture toughness values. The diametral compression test will be used to develop information about the tensile strength of the CCF bond.

2.2.2.1 Subtask 2B-1 -- Flexural Testing to MIL-STD-1942

Four-point bend testing to MIL-STD-1942 is widely applied and accepted. The standard details well-defined surface preparation, which is important for providing valid comparison among materials. Specimens will be sent to experienced outside vendors for preparation. In-house, as-fired specimens will be extensively tested as part of the exploratory and development effort.

Most ambient testing will be conducted in-house, and elevated temperature testing will be conducted by a properly equipped, experienced vendor.

2.2.2.2 Subtask 2B-2 -- Short Rod Fracture Toughness Testing

ATL is equipped with a Terratek Fractometer I System 4201 test apparatus. This will test fracture toughness according to ASTM Standard B-771, Standard Test Method for Short Rod Fracture Toughness of Cemented Carbides. An advantage of this test is that specimens can be readily produced in-house. The method appears to offer a reproducible way to obtain reportable fracture toughness data for ceramic materials.

2.2.2.3 Subtask 2B-3 -- Fracture Testing of Joints

A standard or widely accepted test for fracture toughness testing of ceramic material bonds is not available. Hence, available fracture toughness test methods as they apply to bonds in laminated ceramic items will be evaluated. It is possible that the short rod test in Subtask 2B-2 will be best, but alternatives will be explored.

2.2.2.4 Subtask 2B-4 -- Diametral Compression Test

The diametral compression test appears to have the potential benefit of providing tensile strength information because fractures can be initiated internally as a result of the stress distribution that prevails in the specimen used in this test. Furthermore, the cylindrical specimens necessary can be core-drilled readily from fired ceramic pieces. In addition, it should be possible to orient the bonded region in laminated pieces along a diametral plane and normal to the test platens. Accordingly, this test method is under serious consideration.

2.2.2.5 Subtask 2B-5 -- Microindentation Fracture Toughness Test

In brittle materials, indentation tests for hardness measurements are apt to be in error due to cracks generated by the indenter. These cracks may be useful in assessing the fracture toughness of the material. Some cursory measurements on CCF materials indicated little promise for achieving reliable fracture toughness values. Therefore, this method was discontinued, and no further work under this subtask is anticipated.

2.2.3 Subtask 2C -- Development of Ceramic Specimens for Laminated Bond Testing

The proprietary CCF process imparts a unique pliability to otherwise nonplastic, green ceramic powders. This pliability allows complex shapes to be fabricated without extremely expensive shaping equipment and tooling. Because the CCF process is sufficiently novel, it is imperative to establish that the CCF process can yield high-quality sintered alumina ceramic material with properties equivalent to those of alumina obtained with the traditional ceramic shaping processes (dry pressing, extrusion, and slip casting).

Since the CCF process differs substantially from the more traditional techniques, it is also necessary to establish the optimum processing procedure so the process is compatible with lamination bonding. However, the lamination operation has to be optimized and detailed procedures established.

Lamination bond quality can be determined by comparing the rupture modulus of monolithic samples with those of lamination bonded samples. If statistically significant differences occur between monolithic and laminated specimens and the laminated specimens are weaker, then the bond interface is inherently weak, and process modifications may be needed to increase bond strength.

2.2.4 Subtask 2D -- Ceramic Matrix Composites Using the CCF Process

Two different ceramic matrix composite systems are being explored by CBSi. The reinforcement of alumina by silicon carbide using the CCF

process is being pursued for a high stress (armor) application. In an exploration of the CCF process applied to a nonoxide material, molybdenum disilicide was selected, and grading experiments and reinforcement using silica glass and possibly silicon carbide are being investigated. Further developments under this subtask will be reported as they occur.

2.3 TASK 3 -- CERAMIC FABRICATION AND MANUFACTURING

The overall goal of CBSi is to fabricate complex ceramic components to demonstrate the applicability of CCF technology for defense purposes. The CCF process has the potential to extend the number and complexity of ceramic components available to the government.

CBSi was to produce three complex ceramic components during the course of this contract. The first of these components, the solid oxide fuel cell, was set aside in January 1990 when it became apparent that, although successful integration of a four-cell electrode stack was achieved, the component was lacking in several respects, including gas tightness and dimensional requirements. Time constraints for the other two components did not warrant continued effort on the solid oxide fuel cell. Work was discontinued to allow efforts to be concentrated on the high-stress component (an armor application) and, with lesser priority, on the model MHD electrode. The latter demonstrates the application of the CCF process to a nonoxide ceramic material since molybdenum disilicide had been selected for the base electrode material. Thus, the principal goal was to establish that the CCF process could be adapted successfully to a nonoxide ceramic through grading and bonding of layers of molybdenum disilicide and silicon dioxide.

2.3.1 Subtask 3A -- Solid Oxide Fuel Cell

A complex, planar, multilayer fuel cell model was to be constructed from stabilized zirconia powder. Initial experiments went well and high quality alumina and zirconia membranes were successfully tape cast. Electrode integration problems were encountered, and it became evident that fabricating a four-stack, flaw-free, visually appealing solid oxide fuel cell model was probably not achievable with the available time and resources. This subtask was, therefore, set aside to concentrate on Subtasks 3B and 3C.

2.3.2 Subtask 3B -- MHD Electrode Fabrication

This task calls for the fabrication of a model MHD electrode based on the design arrived at in Subtask 1A. Because molybdenum disilicide was selected to be the material of construction, this subtask demonstrates three features of the CCF process:

- its applicability to a nonoxide material;
- its ability to fabricate layered structures; and
- its ability to fabricate composite (graded) layers.

Due to time constraints, this subtask was determined to be of lesser priority than Subtask 3C, but some work on it is proceeding.

2.3.3 Subtask 3C -- High Stress Component Fabrication

The principal emphasis for this subcontract has now focused on production of CCF process ceramic plates for ballistic testing. Thus, this subtask is where the most effort will be concentrated. The plates will be alumina and a silicon carbide-reinforced alumina. Demonstration curved shapes will be made if there is sufficient time.

3.0 PROJECT STATUS

3.1 TASK 1 -- CERAMIC COMPONENT DESIGN AND ANALYSIS

3.1.1 Subtask 1A -- MHD Electrode Design and Analysis

It was reported previously that molybdenum disilicide was chosen as the electrode material because of its oxidation resistance and high temperature electronic conductivity. However, its brittleness makes it susceptible to thermal shock failure. To solve this problem, grading with a much lower thermal expansion coefficient material, silica glass, was proposed. Modeling studies were conducted using finite element analysis to determine a structure that could withstand the calculated transient as well as steady-state thermal stresses. For this purpose, handbook values for molybdenum disilicide were used, and properties of the graded compositions were computed by the rule of mixtures. A layered structure consisting of 11 layers of molybdenum disilicide with silica glass additions of up to 15 percent was designed and analyzed. During this quarter, the electrical conductivity was rechecked for the calculated temperature gradient to verify that the Joule heating contribution was negligible relative to the temperature gradient due to combustion and cooling conditions. Further refinement cannot be done until a model structure is fabricated and some mechanical tests can be carried out on the graded molybdenum disilicide.

3.1.2 Subtask 1B -- High Stress Component Design and Analysis

No modeling or design work has been carried out. As reported in Section 3.3.3, CBSi has been fabricating ballistic plates, and modeling will not be feasible until an approximate structure and properties have been defined.

3.2 TASK 2 -- EXPLORATORY DEVELOPMENT USING THE CCF PROCESS

3.2.1 Subtask 2A -- Characterization of Starting Materials

No further data was gathered this quarter.

3.2.1.1 Subtask 2A-1 Ceramic Process Control Studies

Due to flaw problems and other processing difficulties encountered while producing specimens, it was decided to conduct a matrix experiment to evaluate the processing parameters. An evaluation was made with regard to six performance factors: sintered density, warpage, blisters, cracks, other surface defects, and relative ease of fabrication. An explanation of the matrix and a discussion of the results are presented in Appendix A.

The Alcoa A16SG alumina did not yield sintered densities as high as those achieved with Reynolds RC-HP alumina. However, the A16SG alumina was chosen previously because it is easily compared with commercial alumina so it was not a variable subject to change. The other six factors proved to have significance more or less in accord with expectations, but, as noted in Appendix A, three-way and higher interactions were assumed to be negligible. Therefore, definite conclusions would have required additional experiments. The principal finding from the matrix experiments, therefore, is that no unanticipated interactions were revealed. Understanding of the importance of the pertinent variables appears to be adequate.

3.2.2 Subtask 2B -- Mechanical Test Methods

3.2.2.1 Subtask 2B-1 -- Flexural Testing to MIL-STD-1942

During this quarter, a batch (lot 68) of MIL-STD-1942 MOR specimens was tested. Some room temperature tests were conducted by MSE and others were done by the subcontractor at the University of Utah. The latter also performed some tests at 1,000 °C. This batch of specimens has a 95 percent theoretical density, somewhat lower than intended. The results are given in Table 1.

These results can be compared with those of higher density materials through use of an empirical equation proposed by Duckworth.¹

$$S = S_0 \exp(-bp)$$

where S is the strength with pores, S_0 is the strength without pores, b is an empirical constant and p is the porosity fraction. Kingery's work² on the flexure strength

TABLE 1 -- FLEXURE STRENGTH AT 21 °C AND 1,000 °C OF LOT 68 MIL-STD-1942
CCF PROCESSED A16SG ALUMINA

NUMBER OF SAMPLES	AVERAGE SINTERED DENSITY	TEST	AVERAGE MOR (ksi)	STANDARD DEVIATION	WEIBULL MODULUS
13	95.0%	25 °C (MCMST)	42.3	13.5%	5.56
35	95.0%	25 °C (U of U)	42.0	7.9%	13.5
22	95.0%	1,000 °C (U of U)	32.3	10.7%	9.3

of alumina provides a value for b of 4.0, which leads to a value of S that is approximately 18 percent less than S_0 for a porosity fraction of 0.05. Applied to the room temperature values in Table 1, the 42 ksi at 0.05 porosity corresponds to about 47.4 ksi at a porosity fraction of 0.02, which is a fairly reasonable value for commercial alumina. The elevated temperature values, if compared with Coors AD999, show an approximate equal strength decline between room temperature and 1,000 °C. This suggests the elevated temperature strength is not affected by the use of the CCF binder system. Testing is to be repeated with higher density material.

3.2.3 Subtask 2C -- Development of Ceramic Specimens for Laminated Bond Testing

During the quarter, the effort to obtain satisfactory test results on laminated samples has been appreciably delayed by problems of reproducibility. Difficulties were encountered in obtaining uniform adhesion over the entire surface of a laminated bond area. The bonding surface of the samples was being altered, but if the reason was contamination, the source was undetermined. The resulting joint would, therefore, contain flaws leading to low test values. Joints were produced in all three possible configurations (see Figure 1). Several parallel joint planes were in the width-depth type specimens and these proved to be the most difficult to produce. This orientation represents the most severe test since bond flaws will be oriented to have the greatest influence on flexure strength, and, with several parallel bond planes, the probability of a strength reducing flaw was high. Future specimens in this orientation will be prepared with only one bond plane located midway through the sample. In-house MOR test results using MIL-STD-1942 type specimens, (as-fired, not machined), yielded values only somewhat lower than monolithic samples from the same batch, suggesting the inherent bond strength was high. However, the monolithic values were substantially lower than those shown to be possible in previous testing. The fabrication of bonded samples is being reexamined to clarify the problem.

Length-Width

Length-Height

Width-Height

FIGURE 1 -- THREE POSSIBLE MIL-STD-1942 FLEXURE STRENGTH TEST BAR JOINT PLANE CONFIGURATIONS

3.2.4 Subtask 2D -- Ceramic Matrix Composites Using the CCF Process

All work in this area is being conducted by CBSi, and in the future, progress for this subtask will be reported in Sections 3.3.2 and 3.3.3.

3.3 TASK 3 -- CERAMIC FABRICATION AND MANUFACTURING

3.3.1 Subtask 3A -- Solid Oxide Fuel Cell

No further work has been conducted on this subtask.

3.3.2 Subtask 3B -- MHD Electrode Fabrication

The modeling and analysis conducted by MSE established that to accommodate the transient and steady-state thermal stresses in the electrode, a graded, multilayered structure was necessary. Although the modeling was based on an 11-layer structure, the immediate objective of this task was to demonstrate fabrication of molybdenum disilicide with graded silicon dioxide at 5 percent intervals from 0:100 to 15:85 (silicon dioxide to molybdenum disilicide) with seven layers arranged symmetrically from 100 percent molybdenum disilicide at the surface to 15 percent silicon dioxide-85 percent molybdenum disilicide in the middle layer.

During the quarter, CBSi concentrated on developing shrinkage and densification data for the different graded chemistries. Sintering aids were explored. Boron oxide, titanium dioxide, and manganese oxide were added at a concentration of 0.6 percent. It was determined that boron oxide aided in the densification of the molybdenum disilicide and assisted in the formation of silica on the surface when the molybdenum disilicide was exposed to air at 1,400 °C. Molybdenum disilicide samples with other additives oxidized without the formation of an adherent surface glass.

When the above aids were added to molybdenum disilicide graded with 15 percent silicon dioxide, all three aids worked well in the 1,400 °C oxidation test. Since boron oxide worked in both the 0 and 15 percent silicon dioxide compositions, it was selected to be the sintering aid for further work.

It was discovered that the manufacturer of the molybdenum disilicide powder inadvertently shipped a stoichiometric blend of molybdenum and silicon, but this powder was found to behave well and to yield molybdenum disilicide after firing. Molybdenum disilicide powder was subsequently obtained and experiments have been conducted on both types. The CCF process works with either type.

XRD and SEM/EDX was used to look at the outer skin formed on sintered pellets. This skin was found to consist of molybdenum-rich and silicon-rich phases. Further work is needed to eliminate the skin formation.

Later in the quarter, the desirable amount of boron oxide was set at 1.4 weight percent as this yielded optimum densities (>85 percent) when sintered at 1,800 °C for 1 to 3 hours. The high temperature part of sintering is carried out in an argon atmosphere with the low temperature part requiring a reducing atmosphere to prevent oxidation of the molybdenum or molybdenum disilicide when passing through the 700 to 1,100 °C interval. The reducing atmosphere is obtained by adding hydrogen to the argon.

To produce molybdenum disilicide layers, different techniques were explored to produce layers by means of a screen printer modified to act as a tape caster. This enabled production of small samples. After firing, the tape cast material has high mechanical integrity, but no MOR specimens could be fabricated. Plates were designed for the screen printer to permit fabrication of seven layers; these have been sent out for procurement.

It was possible to prepare 0.5-inch span, three-point bend test samples from pressed disks that were fabricated and sintered 2 hours at 1,800 °C in argon. Five samples gave an average value of 27.7 ksi (193 MPa). The literature value for the flexure strength of molybdenum disilicide at room temperature appears to be about 23.2 to 25.4 ksi (160 to 175 MPa) for high density material (95 to 98 percent).

3.3.3 Subtask 3C -- Fabrication of High Stress Component

As noted in Section 2.3.3 the focus of this task is the fabrication of CCF ballistic test plates from alumina and from a composite plate of alumina reinforced with silicon carbide platelets. Some previous experiments were done with silicon carbide whiskers, but, not only are whiskers too expensive for practicable low cost production, they inhibit densification and virtually necessitate hot-pressing or HIPing. Even platelets restrict densification, and since the CCF process involves pressureless sintering, one of the first steps in this subtask was to investigate sintering aids as noted in the January 1 to March 31, 1990, Quarterly Report.

A supply of 23- μ m platelets having an aspect ratio of 8:10 was obtained from C-Axis, Inc. Two smaller diameters are manufactured but were not immediately available.

To determine the optimum platelet loading, an initial pressed pellet test series was performed. Tridoped alumina containing 2 weight percent total of titanium dioxide, manganese dioxide, and iron oxide in equal proportions was used as the base material. Densities of 95.5 to 96.0 percent theoretical were found to be achievable when fired in air or argon at 1,600 °C for 2 hours. Pressed pellets made from doped alumina (Reynolds RC-HP) containing four levels of silicon carbide, viz., 5, 10, 15, and 20 percent by weight were fired at 1,600 °C for 2 hours. The respective densities were 95.5, 93.8, 90.2, and 84.7 percent of theoretical (see Figure 2).

FIGURE 2 -- RC-HP, TRIDOPED SAMPLES, 0 TO 20 WT% SiC PLATELETS

Diametral compression (DC) tests were carried out on pellets, and the 10 percent silicon carbide loading showed the highest strength at 9 ksi (see Figure 3). In a comparison of nonplatelet containing tridoped alumina with 15 percent silicon carbide tridoped alumina (see Figure 4) in DC testing, the straight alumina tested at 11.2 ksi, and the 15 percent silicon carbide material tested at 6.6 ksi. A DC test on commercial, 98.6 percent dense, isostatically pressed alumina gave 18 ksi.

Microstructural examination showed evidence of crack deflection at platelet interfaces and an absence of preferred platelet orientation. It was also observed that large pores were developing during sintering, and subsequent investigations indicated that the manganese dioxide component of the tridoped sintering aid was reacting with the silicon carbide platelets during high temperature processing.

Ballistic test plates must be either 4 by 4 by ≈ 0.5 inches (U. Dayton, Impact Physics Laboratory) or 6 by 6 by 1 inch (Aberdeen Proving Grounds). Hence, efforts to produce thick plates were initiated. It was necessary to adjust the standard CCF process because of difficulties in achieving thick shapes with the standard procedure. A large alumina piece, approximately 2 by 4.5 by 7 inches and weighing approximately 3.5 kg, was produced and fired. The piece was too large for density measurement in the usual way but was judged to be 86 to 88 percent dense. The piece debindered and fired without difficulty, but it was evident that it had significant internal pores. From this and other similar such pieces, it became apparent that removing entrapped air was necessary to improve quality and density. To this end, a used pug mill was acquired toward the end of the quarter. It will be cleaned and placed in service. The pug mill enables a vacuum to be pulled on the batch prior to its extrusion to air, so efficient deairing of a batch should be possible.

4.0 PLANNED ACTIVITIES

4.1 TASK 1 -- CERAMIC COMPONENT DESIGN AND ANALYSIS

4.1.1 Subtask 1A -- MHD Electrode Design and Analysis

The electrode design has been based on property data available in literature, which relates largely to hot-pressed material. Very limited high temperature data was found. The design will be refined if property data pertaining to CCF processed molybdenum disilicide (which will be less than 100 percent dense) can be obtained before the end of the contract. There are no plans to measure high temperature properties.

FIGURE 3 -- RC-HP, TRIDOPED SAMPLES, 0 TO 20 WT% SIC PLATELETS (Diametral Compression Measurements)

FIGURE 4 -- RC-HP, TRIDOPED SAMPLES, 10 WT% SiC PLATELETS (Diametral Compression Measurements)

4.1.2 Subtask 1B -- High Stress Component Design and Analysis

No activity is planned during the next quarter.

4.2 TASK 2 -- EXPLORATORY DEVELOPMENT USING THE CCF PROCESS

4.2.1 Subtask 2A -- Characterization of Starting Materials

No activity is planned during the next quarter.

4.2.2 Subtask 2B -- Mechanical Test Methods

4.2.2.1 Subtask 2B-1 -- Flexural Testing to MIL-STD-1942

Further testing is planned to obtain data on specimens laminated and monolithic specimens (minimum 97 percent dense) at room temperature and 1,000 °C.

4.2.2.2 Subtask 2B-2 -- Short Rod Fracture Toughness Testing

Testing is planned for the next quarter.

4.2.2.3 Subtask 2B-3 -- Fracture Testing of Joints

Testing is planned for the next quarter.

4.2.2.4 Subtask 2B-4 -- Diametral Compression Test

Testing is planned for the next quarter.

4.2.2.5 Subtask 2B-5 -- Microindentation Fracture Toughness Test

Work under this subtask has been discontinued; therefore, reporting will be suspended.

4.2.3 Subtask 2C -- Development of Laminated Ceramic Specimens for Testing

Reexamination of the fabrication procedure for laminated specimens is planned. The objective is to obtain reasonably flaw-free, high density laminates from which MIL-STD-1942 specimens can be machined.

4.2.4 Subtask 2D -- Ceramic Matrix Composites Using the CCF Process

This work will be carried out by CBSi.

4.3 TASK 3 -- CERAMIC FABRICATION AND MANUFACTURING

4.3.1 Subtask 3A -- Solid Oxide Fuel Cell

No further work on this subject is planned.

4.3.2 Subtask 3B -- MHD Electrode Fabrication

Priority has been given to Subtask 3C, so the goal of this subtask is the production of a three-layer graded molybdenum disilicide component. Grading will be proven using a suitable x-ray line profile or map. Mechanical test data and microstructural characterization will be carried out.

4.3.3 Subtask 3C -- High Stress Component Fabrication

Principal efforts will be focused on this subtask during the next quarter. The goal is to produce plates that can go to ballistic testing. Dimensions have to be 4 by 4 by ≈ 0.5 inches, and plate has to be square and flat. The plate will be characterized before ballistic testing.

5.0 TECHNICAL SUMMARY

5.1 TASK 1 -- CERAMIC COMPONENT DESIGN AND ANALYSIS

Very little additional work was carried out. Verification of the negligible contribution of Joule heating to the graded, layered structure was carried out using literature values of conductivity. Design work is on hold until actual experimental values can be supplied.

5.2 TASK 2 -- EXPLORATORY DEVELOPMENT USING THE CCF PROCESS

Results of the matrix (ANOVA) experiments indicate that understanding of the effects of the CCF process variables is satisfactory. It was reasonably assumed that three-way and higher interactions were negligible.

Results of 1,000 °C MOR tests suggest that the elevated temperature properties of alumina are not degraded by the CCF process.

Difficulties were encountered in the fabrication of satisfactorily bonded specimens for testing, and MIL-STD 1942 data is not yet available.

5.3 TASK 3 -- CERAMIC FABRICATION AND MANUFACTURING

Both molybdenum disilicide and elemental molybdenum and silicon powders in stoichiometric ratios were used with the CCF binder system to yield

molybdenum disilicide specimens. Efforts concentrated on developing sintering aids to assist the achievement of high sintered densities in the pressureless sintering characteristic of the CCF process. Elemental boron at the 1.4 percent level gave densities in the 85 percent theoretical range when sintered at 1,800 °C. It was found necessary to use a hydrogen atmosphere up to around 1,100 °C and then to switch to argon between 1,100 and 1,800 °C. It was found possible to conduct some in-house three-point bend tests on small molybdenum disilicide pieces. These gave results that compared well with literature values.

A source of SiC platelets was determined, and a supply of 23- μ m diameter platelets was obtained. Work on sintering aids for platelet-loaded alumina was pursued.

The problems in producing thick test plates (4 by 4 by 0.5 inches) suitable for ballistic tests were tackled by exploring various modifications to the CCF process and various routes to the desired shapes. Deairing and debinding were reinvestigated. At the end of the quarter, a pug mill was acquired, and it should control the deairing problem.

6.0 REFERENCES

1. "Discussion of Ryshkewitch Paper," Duckworth, W., Journal of American Ceramic Society; 1953, 36(2) 68.
2. "Effect of Porosity on Physical Properties of Sintered Alumina," Kingery, W.D., Journal of American Ceramic Society; 1956, 39(11) 377-385.

APPENDIX A -- Interpretation of Results of Matrix Experiments

A one-eighth replicant of a seven-factor factorial design of resolution four was used in designing the experimental statistical matrix. This matrix consists of 16 experimental runs. Table A1 shows the statistical experimental plan, and Table A2 defines the factors and the significance of the + and - symbols.

TABLE A1 -- STATISTICAL EXPERIMENTAL PLAN

EXPERIMENTAL RUN NUMBER	FACTORS (Experimental Variables)						
	A	B	C	D	E	F	G
16	-	-	-	-	-	-	-
7	+	-	-	-	-	+	+
6	-	+	-	-	+	-	+
13	+	+	-	-	+	+	-
12	-	-	+	-	+	+	+
3	+	-	+	-	+	-	-
2	-	+	+	-	-	+	-
9	+	+	+	-	-	-	+
8	-	-	-	+	+	+	-
15	+	-	-	+	+	-	+
14	-	+	-	+	-	+	+
5	+	+	-	+	-	-	-
4	-	-	+	+	-	-	+
11	+	-	+	+	-	+	-
10	-	+	+	+	+	-	-
1	+	+	+	+	+	+	+

TABLE A2 -- EXPLANATION OF TABLE A1

FACTOR	(+)	(-)
A	Sigma Mixing	Fiber Spinning
B	Calendaring	Extrusion
C	RC-HP Alumina	A16SG Alumina
D	Low Amount Binder	Regular Amount Binder
E	Regular Amount Reagent T	High Amount Reagent T
F	27-hr Browning Cycle	56-hr Browning Cycle
G	Low Air Flow in Browning Cycle	High Air Flow in Browning Cycle

Sigma mixing refers to the procedure for mixing the binder ingredients with the alumina powder by mixing everything, with added acetone as solvent, in a sigma mixer. The acetone is removed using a vacuum applied to the sigma mixer vessel. The product is a green CCF alumina mass, which has to be formed into some convenient shape. Fiber spinning refers to an alternative way to mix the binder ingredients into the alumina. It entails ball-milling the alumina and the binder ingredients with acetone as solvent. The acetone is removed in a spin drying process, which yields fibrous alumina aggregates. These aggregates have to be consolidated into convenient shapes.

Calendaring refers to rolling the mixed ceramic to yield a thin slab or plate of green ceramic. It can be carried out on either of the products of sigma mixing or fiber spinning. Similarly, extrusion refers to placing a batch of mixed ceramic in a container in a press, applying a vacuum to deair the mix, followed by operating the press to extrude a plate or slab.

The samples from each experiment were rated on six different criteria: density, warpage, blistering, cracking, other surface flaws, and ease of formation.

The measured sintered density is recorded as its percentage of theoretical density; therefore, the closer the density is to 100 percent, the better the sample. For the other five criteria, warpage, blistering, cracking, other surface flaws, and ease of formation, a different rating system was developed. The samples were rated from zero to five in each category, zero being the best rating and five the worst. Thus, 0 - No evidence of particular flaw; 2 - Sample okay, but definitely has some flaws; 5 - Bad sample with obvious large flaws.

With a one-eighth replicant, there is always a large degree of confounding between the various effects. In a resolution four design, such as this one, the main effects (A, B, C, D, E, F, and G) are confounded only with three-way and higher interactions. Consequently, it was assumed that all three-way and higher interactions were insignificant.

For each rating criterion, Yates' algorithm was applied to obtain the mean effect, the estimated effects, and their corresponding sum of squares (SSQ). The smallest effects were assumed insignificant and their SSQ's were collected together to form an estimate for the error SSQ. From this information, an analysis of variance (ANOVA) table was constructed to determine which of the remaining effects were truly significant at the 5 percent level of confidence. A summary of the results obtained from this statistical analysis appears below for each of the six different rating criteria.

Theoretical Density

From the Yates algorithm and the ANOVA table, the significant main effects were found to be A, B, C, E, and F. The above factors are listed below in their order of significance (from most significant to least significant). For each factor the level having the most beneficial effect on the sintered density is underlined.

C - <u>RC-HP Alumina</u>	vs. A16SG alumina
B - <u>Calendaring</u>	vs. Extrusion
E - <u>Reagent T, regular Amount</u>	vs. High Amount Reagent T
F - <u>27-hr Browning Cycle</u>	vs. <u>56-hr Browning Cycle</u>
A - Sigma Mixing	vs. <u>Fiber Spinning</u>

Of the interactions, the BE + AF interaction had the most significant effect on the sintered density.

Warpage

Listed below are the most significant main effects for warpage. Factors C and F were most significant, followed by A and G. The level that reduces warpage for each factor is underlined.

C - RC-HP Alumina	vs. A16SG Alumina
F - <u>27-hr Browning Cycle</u>	vs. 56-hr Browning Cycle
A - Sigma Mixing	vs. <u>Fiber Spinning</u>
G - <u>Low Air Flow (Browning)</u>	vs. High Air Flow (Browning)

Of the interactions, the AG interaction was the most significant; in fact, it was more significant than any of the main effects.

Blistering

For blistering, the most significant main effect was B, followed by effects A, D, and F, each having the same level of significance. For each of these factors, the level that reduced blistering is underlined.

B - Calendaring	vs. <u>Extrusion</u>
A - Sigma Mixing	vs. <u>Fiber Spinning</u>
D - <u>Low Amount Binder</u>	vs. Regular Amount Binder
F - 27-hr Browning Cycle	vs. 56-hr Browning Cycle

The following two-way interactions also had significant effects on blistering: AB, BD, and BF.

Cracking

For cracking, the most significant main effects are D and F, followed by effects A and E. For each significant main effect, the level that reduces cracking is underlined.

D - Low Amount Binder	vs. <u>Regular Amount Binder</u>
F - 27-hr Browning Cycle	vs. <u>56-hr Browning Cycle</u>
A - <u>Sigma Mixing</u>	vs. Fiber Spinning
E - Regular Amount Reagent T	vs. <u>High Amount Reagent T</u>

Overall, the most significant effect on cracking was a two-way effect, the DF interaction.

Other Surface Flaws

Main factor D had the most significance, followed by factors G, A, and E. The underlined levels have a reducing effect on all other surface flaws.

D - Low Amount Binder	vs. <u>Regular Amount Binder</u>
G - <u>Low Air Flow (Browning)</u>	vs. High Air Flow (Browning)
A - Sigma Mixing	vs. <u>Fiber Spinning</u>
E - Regular Amount Reagent T	vs. <u>High Amount Reagent T</u>

Of the two-way interactions, DE + AG had the most effect on the surface flaws.

Ease of Forming

The ease of formation was most significantly affected by main factor D, followed by factors B and E, which were judged to be equally significant. The underlined levels for each of these factors indicates the methods or options that conferred easier forming of specimens.

D - Low Amount Binder	vs. <u>Regular Amount Binder</u>
B - Calendaring	vs. <u>Extrusion</u>
E - Regular Amount Reagent T	vs. <u>High Amount Reagent T</u>

The two-way effect that was most significant to ease of forming was the DE interaction.

It was observed that certain procedures or options were more beneficial overall to increased density and to reduction in sample flaws in the experiments. The obviously beneficial methods included: the use of RC-HP alumina over Al6SG alumina, fiber spinning rather than Sigma mixing, and a longer (56 hr) browning cycle versus a short (27 hr) browning cycle.

Because a fractional experimental design was used, the estimate for each effect is compounded with other effects, thus, making it impossible to determine all of the interaction effects. Therefore, additional experiments are needed before definitive conclusions can be reached concerning which factors and interactions are most beneficial to the CCF process.

APPENDIX B -- Project Schedule

MSE, Inc.

CERAMICS PROJECT PROJECT MANAGEMENT

CURRENT STATE

PLANNED SCHEDULE

TASK I - DESIGN AND
ANALYSIS OF CERAMIC
COMPONENTS

MSE, Inc.

TASK II - EXPLORATORY
DEVELOPMENT USING
CCF PROCESS BOND

MSE, INC.

CERAMIC BINDER SYSTEMS, INC

TASK III - CERAMIC FABRICATION

PLANNED SCHEDULE

CURRENT STATE

CERAMIC R&D FOR DEFENSE APPLICATIONS

CERAMIC R&D FOR DEFENSE APPLICATIONS

CERAMIC R&D FOR DEFENSE APPLICATIONS

CERAMIC R&D FOR DEFENSE APPLICATIONS

CERAMIC R&D FOR DEFENSE APPLICATIONS

DESCRIPTION	FY-89						FY-90											
	MAY	JUN	JUL	AUG	SEP		OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP
MISE - PROJECTED	5,040	24,480	41,000	68,230	95,170		120,880	145,840	171,040	197,280	222,480	247,980	273,270	298,720	324,000	349,240	374,970	400,000
MISE - ACTUAL	4,800	20,300	34,480	56,203	74,309		90,279	109,486	128,063	145,767	160,242	181,179	205,576	262,697	322,441			
ATL - PROJECTED	600	17,106	55,400	135,600	192,300		239,300	282,600	327,300	378,200	422,400	470,000	515,400	563,000	608,900	608,900	608,900	608,900
ATL - ACTUAL	600	15,573	32,188	67,749	78,847		91,522	132,274	160,636	211,188	247,503	295,977	349,352	360,568	360,568			
CBS - PROJECTED	940	11,870	30,170	51,580	80,240		103,350	126,480	148,630	174,980	197,820	220,120	242,420	264,180	285,940	307,340	328,670	350,000
CBS - ACTUAL	940	15,393	37,432	56,074	69,779		81,329	95,974	113,864	135,443	159,676	184,337	211,619	238,180	281,440			
TOTAL - PROJECTED	6,580	53,450	126,570	255,420	367,710		463,340	554,900	646,970	750,460	842,710	938,110	1,031,080	1,125,900	1,218,840	1,265,480	1,312,540	1,358,900
TOTAL - ACTUAL	6,340	51,266	104,088	180,026	222,935		283,130	337,734	400,599	482,398	567,421	661,483	766,547	861,445	964,449			

NOTE: ATL operations were merged with MSE during May of 1990.

END

DATE FILMED

02 / 15 / 91