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QUARTERLY TECHNICAL PROGRESS REPORT

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EXECUTIVE SUMMARY

The project is separated into three tasks. The first task is a design and modeling effort to be carried out by MSE, Inc. The initial undertaking of Task 1 is the design of an advanced ceramic MHD electrode.

The second task, subcontracted to Applied Technology Laboratories (ATL), is directed at characterizing the mechanical properties of monolithic and bonded ceramics produced with the cohesive ceramic fabrication (CCF) process.

The third task, subcontracted to Ceramic Binder Systems, Inc. (CBSi), is to fabricate the components designed in Task 1 and to fabricate a model planar solid oxide fuel cell.

These tasks are discussed separately in this report.

Areas of technical progress included in this first quarterly report are:

- assessing design specifications for a hot ceramic MHD electrode;
- reviewing components suited for CCF process design demonstration;
- transferring the CCF process technology from CBSi to MSE and ATL personnel;
- reviewing test methods suited to characterizing mechanical properties of CCF process ceramics; and
- fabricating individual components for a planar solid oxide fuel cell.

Task 1 is attempting to search out high temperature property data for the exotic ceramics under consideration. This task is consuming more effort and time than originally anticipated.

Task 2 encountered dimensional and shape control problems when thicker parts were attempted, necessitating a review of the details of the fundamental steps in the CCF process. Laboratory renovations and equipment acquisitions have been completed, and most staffing is completed. Considerable effort is being devoted to bringing this task back on schedule.

Task 3 has made good progress and is on schedule.

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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 the components that will be fabricated to demonstrate the applicability of the CCF process to defense systems: including an MHD electrode for strategic defense initiative (SDI) applications and an as-yet-to-be-identified high stress component.

This task is the principal responsibility of MSE, Inc.

2.1.1 SUBTASK 1A -- MHD ELECTRODE DESIGN AND ANALYSIS

The overall thrust of this subtask is to design a ceramic MHD electrode with advanced characteristics using the unique capabilities of the CCF process.

An initial design will be generated based on input from MHD and materials specialists and design requirements related to defense power system 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 the electrode design used as the basis for fabricating the MHD 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. Candidate high stress components include armor, automotive components, heat exchangers, and an MHD electrode complex.

The design and analysis approach will be similar to that used in Subtask 1A, in that design requirements will be generated, designs formulated to meet those requirements, and then they will be analyzed using finite element techniques.

2.1.3 SUBTASK 1C -- PROJECT MANAGEMENT

This subtask entails managerial and technical supervision of all Task 1 work as well as oversight, technical and general monitoring of Task 2, which is subcontracted to Applied Technology Laboratories (ATL), a division of Montana Technology Companies, and of Task 3, which is subcontracted to Ceramic Binder Systems, Inc. (CBSi).

This subtask covers reporting technical progress and tracking contract expenditures and work schedules.

2.2 Task 2 -- Exploratory Development Using the CCF Process

This task deals with developing and testing ceramic materials produced with the CCF process. 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 starting materials is planned because it is anticipated that manufacturer's specifications and data will be adequate for most purposes. Some chemical and microstructural testing will be carried out.

2.2.2 SUBTASK 2B -- MECHANICAL TEST METHODS

Flexure testing according to MIL-STD-1942 is widely practiced and accepted. This testing will be adequate for determining the strength of monolithic parts produced using the CCF process. A similar test for evaluating the bond strength between ceramic parts does not exist. Though bonded parts will be tested to MIL-STD-1942, a review of possible test methods is planned.[1] Some fracture toughness tests will be evaluated and some testing will be done.

2.2.3 SUBTASK 2C -- FLEXURAL TESTING TO MIL-STD-1942

Four-point bond 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.

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

2.2.4 SUBTASK 2D -- 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]

2.2.5 SUBTASK 2E -- 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 may apply to bonds in laminated ceramic items will be evaluated. It is possible that the short rod test above will be best, but alternatives will be explored.

2.2.6 SUBTASK 2F -- 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.

2.2.7 SUBTASK 2G -- DEVELOPMENT OF CERAMIC SPECIMENS FOR LAMINATED BOND TESTING

This subtask requires that ATL technicians and staff be disclosed to and trained in the proprietary CCF technology by the staff and technicians of CBSi. Once this is adequately and satisfactorily accomplished, the ATL personnel can establish procedures and routines for fabricating shapes from which suitable specimens can be cut or otherwise prepared.

The process involves selecting an alumina powder that will be the basis for test reports. The proprietary binder formulation has to be mixed into the powder (by a procedure yet to be established), and uncured (green) shapes are subsequently produced. The process of debindering initially yields a brown (partially debindered) state that is characteristically rigid and machinable but may be relatively soft and deformable. In the brown state, most but not all binder has been driven off. Specimens may be more readily cut in the brown state. Firing converts the brown state to the fired state, and all binder is totally driven off.

Laminated joints or bonds are readily produced in the green state with only light pressure, corresponding to hand pressure, being needed. This is a consequence in part of the tackiness of the green state. Bonds are also easily produced between browned parts via the interposition of a green layer. Upon firing, the bond region is indistinguishable microstructurally from the base material.

This subtask will focus on the production of specimens designed to yield information about the strength of the bonds produced by laminating as indicated above. The microstructure of the bonded regions will be characterized, and the fracture toughness of the bonded regions will be evaluated.

2.3 Task 3 -- Ceramic Fabrication and Manufacturing

The overall goal of CBSi is to fabricate complex ceramic components that may be used to demonstrate CCF technology. This CCF technology has the potential to dramatically extend the number and the complexity of ceramic components available to the government. Furthermore, the near-term goal of the proposed work is to produce complex ceramic shapes that have near-term applicability to the Department of Defense.

CBSi will produce three complex ceramic components during the course of this contract. The first component is a complex model of a solid oxide fuel cell, the second is an advanced concept MHD electrode, and the third is a high stress component of unknown specification.

2.3.1 SUBTASK 3A -- SOLID OXIDE FUEL CELL

The solid oxide fuel cell (SOFC) is a planar fuel cell design. The planar design is useful because it allows a higher density membrane area than other solid oxide fuel cell designs. In this task, a complex, multilayer fuel cell model will be fabricated using a stabilized zirconia powder. Although a complex shape will be produced, the SOFC model will not function as a fuel cell, because this is a demonstration ceramic fabrication model, not an actual, operable fuel cell. The difference being the CBSi fuel cell will be fabricated from a single oxide material; it will not have fuel electrodes, air electrodes, or interconnector materials--all of which are needed for actual operation.

2.3.2 SUBTASK 3B -- MHD ELECTRODE FABRICATION

The second component to be fabricated by CBSi is an advanced MHD hot ceramic electrode. The electrode is to be designed by MSE with collaboration and support from CBSi. Analysis and modeling will be done by MSE after which the design will be turned over to CBSi for fabrication.

2.3.3 SUBTASK 3C -- HIGH STRESS COMPONENT FABRICATION

The third component to be fabricated by CBSi is a ceramic component that experiences a high stress, either thermal or mechanical, while in service. This component is to be selected by MSE with CBSi collaboration. Analysis and modeling will be done by MSE, and the design will be turned over to CBSi for fabrication.

3.0 PROJECT STATUS

3.1 Task 1 -- Ceramic Component Design and Analysis

The initial effort in this subtask was to explore the feasibility of using the CCF process to design and fabricate an advanced MHD electrode incorporating integral electronic switching capabilities. Evaluation of current technology of semiconducting ceramics suggests integral switching capabilities are not feasible within the design parameters for the MHD electrode. These parameters are those pertinent to defense power system applications.[3]

Attention is now focusing on a hot ceramic MHD electrode to which conventional electronic components could be attached.

Various options for the high stress component in Subtask 1B have been identified, and others are being explored.

3.1.1 SUBTASK 1A -- MHD ELECTRODE DESIGN AND ANALYSIS

Modeling and analysis are now underway. Estimates of temperature distribution for assumed geometries are being carried out so a fix on dimensions can be made. Tungsten and zirconia properties are currently being used; however, a final choice of materials has not been made. Tungsten is a reasonable thermal expansion match to many ceramics, but other metals, including graphite and silicon carbide, are being considered. Thermal and electrical conductivities are not well characterized for many materials at the temperatures attained in the hot side of the MHD electrode. The same is true for the temperature dependence of the elastic modulus and thermal expansion.

3.1.2 SUBTASK 1B -- HIGH STRESS COMPONENT DESIGN AND ANALYSIS

In this subtask, a high stress ceramic component is to be designed. This component could be, for example, ceramic tile used in armor applications for personnel protection, either as body armor or incorporated into aircraft seats.

Such armor is often a composite material such as silicon or boron carbide fibers, platelets, or particles dispersed in a matrix of alumina. The CCF process would allow the production of multilayers wherein a controlled orientation of the platelets or fibers could be arranged in each layer. Conventional production of this type of material involves hot-pressing, which yields high density and strength material but is unfortunately an expensive process and not one which lends itself to high production rates. It is uncertain whether controlled orientations of the dispersed phase are feasible.

The CCF process appears to offer complex composite shape fabrication without hot pressing, although it remains to be demonstrated whether these acceptably high densities can be readily achieved.

An alternative component for this task would be a complex MHD electrode wall segment wherein a number of ceramic electrodes each separated with an insulator but joined into a monolithic piece would be fabricated. Yet another possibility is a ceramic heat exchanger tube for application in the University of Tennessee Space Institute hot seed recovery system. A very steep temperature gradient can exist across the tube, and the presence of coal slag and seed characterizes this application. It appears to be one well suited to the property grading capabilities of the CCF process.

No firm decision on this component was planned for this quarter, and it is possible that the Defense Advanced Research Project Agency (DARPA) may have some input on the above items or on some other ceramic item that may be suited to the CCF process. Definition of the high stress component is planned for early in the next quarter.

3.1.3 SUBTASK 1C -- PROJECT MANAGEMENT

Detailed work plans were substantially completed by the end of July. Actual experimental work got underway immediately upon signing of the subcontract at CBSi, and good progress has been made because facilities and manpower were already available. At ATL, it was necessary to renovate some laboratory space and add professional and technical staff. This could not proceed until the subcontract had been signed. Transfer of the CBSi CCF technology to ATL staff was performed immediately after the subcontract and necessary disclosure agreements were signed.

The exploratory development to be undertaken by ATL has to produce reliable strength data. Given the inherent nature of mechanical property data resulting from tests on brittle solids, data scatter attributable to processing variables must be eliminated to the extent possible. For this reason, a sigma-type mechanical mixer that would permit thorough and reproducible mixing and could operate with a vacuum to eliminate air bubbles and, thus, defects was procured. Due to the inherently stiff nature of the ceramic/binder mix, a relatively high horsepower-to-capacity ratio mixer was needed. The difficulty in obtaining a laboratory-sized mixer caused schedule delays for ATL.

3.2 Task 2 -- Exploratory Development Using the CCF Process

Task 2 is behind schedule for various reasons, including laboratory renovation delays and problems with equipment acquisition and staffing. Technology transfer of the CCF process from CBSi has been accomplished, and efforts are underway to develop batch preparation methods that will yield satisfactory MOR bars. The powder and binder have been characterized, testing methods have been investigated and selected, and staffing continues.

3.2.1 SUBTASK 2A -- CHARACTERIZATION OF STARTING MATERIALS

Certificates of analysis have been and will be requested for all materials ordered including ceramic powders and binder components. In general, these certificates provide only quality control data, which may include chemical analytical as well as other data. Further data has also been requested.

In the case of the alumina powder received, Alcoa A-16SG, the BET surface area, 8.6 cm^2/g, and Mg content, 0.03 percent, were provided by Alcoa. A Sedigraph curve (particle-size distribution) is to be supplied. However, Sedigraph curves routinely provided by Alcoa are for powders dispersed by ultrasonic probe. Hence, powder agglomerates are broken up. This provides more basic, more reproducible data, independent of the agglomerate distribution. The particle size distribution of A-16SG is given by Alcoa to be 0.3 to 0.5 μm.

For the present characterization, the particle-size distribution after ultrasonic probe treatment appears to be relevant, as ball milling will change distributions that include agglomerates. The particle-size distribution entering the CCF process after ball milling is unknown.

For the purposes of this project and for manufacturing dense strong alumina in general, removing powder agglomerates can be expected to improve strength, as agglomerates tend to sinter rapidly, leaving void shells that can provide large critical defects (i.e., low strength data). Consequently, for A-16SG, ball milling to remove agglomerates is prescribed by CBSi to provide what is expected to be the best material.

3.2.2 SUBTASK 2B -- MECHANICAL TESTS METHODS

Mechanical testing is required to characterize the materials and joints prepared by the CCF processes. Reliable data requires large numbers of test specimens due to the brittle nature of ceramics and the effects of processing flaws.

The bonds will be developed in shapes especially designed to be suitable for fracture testing. Generally, the test specimens must be cut from the shapes. Comparison of joint fracture strengths and fracture toughnesses with strengths and toughnesses of the materials joined will provide some indication of the quality and usefulness of the joints. The choice of fracture test methods is discussed below.

In general, the test methods can be applied to single- and dual-layered structures. Some testing of multiple-layered structures can be provided by the four-point bend flexure test, which is the primary materials test to be applied.

3.2.3 SUBTASK 2C -- FLEXURAL TESTING TO MIL-STD-1942

Flexural testing, especially by the four-point bend test, is widely applied and accepted and is a generally applicable strength test for ceramic materials. Testing by proposed MIL-STD-1942[4] is most applicable to ceramics. This standard details well-defined surface preparation, which is important for providing valid comparison among materials. This test is expected to be approved as an ASTM standard within a year or less.

A fixture (shown in Figure 1) designed for flexure testing according to MIL-STD-1942 was purchased from MTS Systems Corporation in Minneapolis, Minnesota.

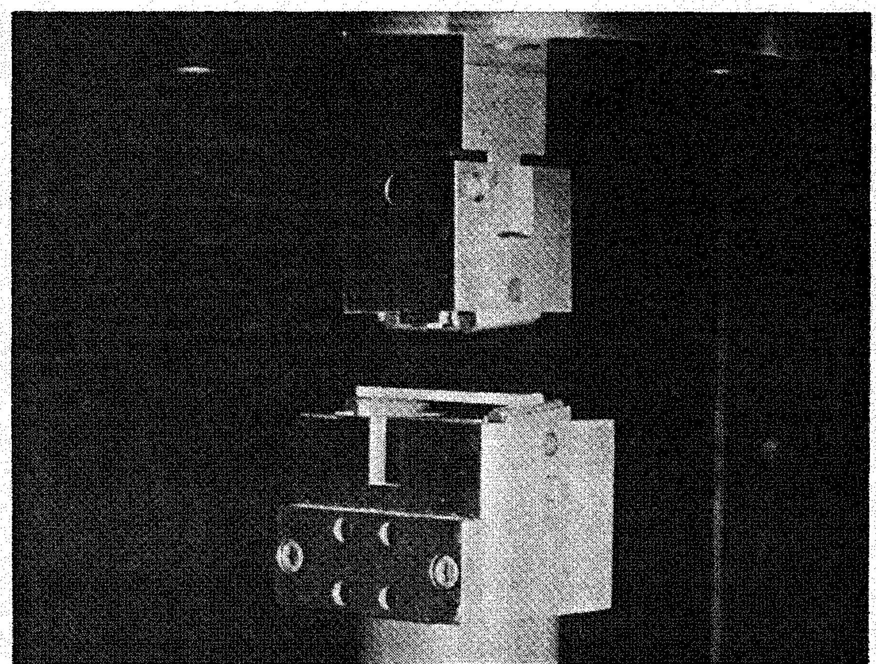


FIGURE 1 -- MTS SYSTEMS CORPORATION FLEXURE TESTING FIXTURE.

This fixture is fully articulated, with three of four rollers free to pivot about the lengthwise axis of the specimen. This feature significantly reduces contact stresses and allows the as-fired specimens with some curvature to be tested. Articulation of the upper loading block, which is in two pieces joined by a pivot pin, further reduces misalignment. These features greatly reduce measured strength variations caused by stress concentrations of misaligned brittle material specimens. This will also improve the confidence in strength results obtained from as-fired test specimens.

The presence and magnitude of bonding flaws such as delaminations will be evaluated by comparing flexure strengths of laminated bars (laminations parallel to the applied force versus laminations normal to the applied force) with monolithic (unlaminated) bars. This strength data will also be compared with fracture toughness measurements.

3.2.4 SUBTASK 2D -- SHORT ROD FRACTURE TOUGHNESS TESTING

According to TerraTek Systems, "ASTM Standard B-771, 'Standard Test Method for Short Rod Fracture Toughness of Cemented Carbides,' has recently been approved and other standards are in process. A TerraTek Fractometer I System 4201 is available. This test has the advantage that specimens can be made readily. This method will provide reproducible and reportable fracture toughness data for monoliths (i.e., for materials prepared by CCF methods).

The Fractometer test system has been developed specifically to measure plane strain fracture toughness ($K_{Ic}SR$) using chevron-notched short rod test specimens. This test method allows measurement of plane strain fracture toughness at reduced testing costs compared with other methods."

The Fractometer I System and the chevron-notched short rod specimen offer a number of advantages:

- Fatigue precracking is not required. Thus, the test procedure is simple and can be applied to brittle as well as ductile materials.
- Small specimen sizes can be used. Specimens may be 50 percent of the thickness and 3 percent of the volume of an ASTM E399 compact tension specimen.
- Test data shows high repeatability. Coefficients of variation for repeated tests on the same material are generally less than three percent.
- Excellent agreement with K_{Ic} has been demonstrated for a wide range of materials.

Figure 2 shows the saw-cut notches in the short rod specimen. Rectangular short bar specimens can also be employed. Short rod specimens for this project will be fabricated from sintered slabs by diamond core drilling.

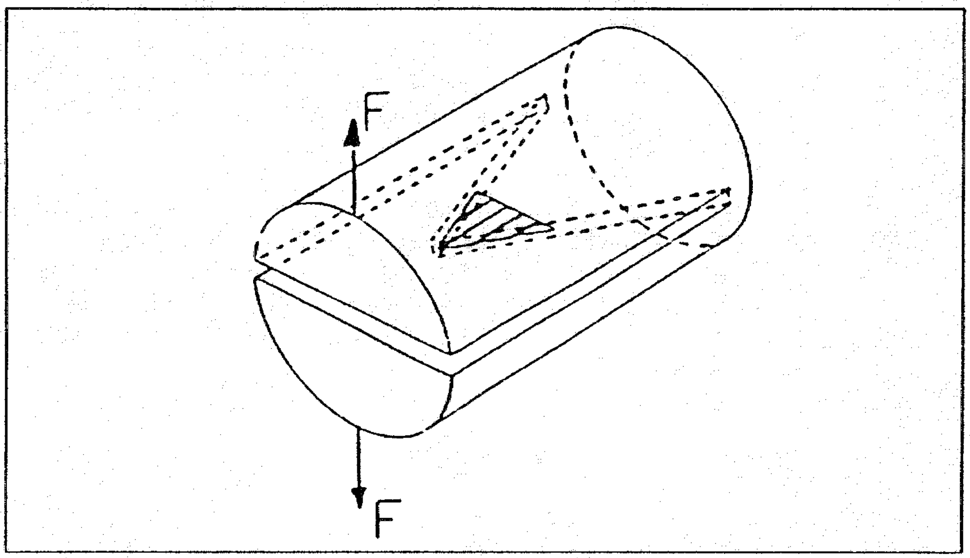


FIGURE 2 -- SHORT ROD SPECIMEN. (THE SHADED AREA DENOTES THE CRACK.)

3.2.5 SUBTASK 2E -- FRACTURE TESTING OF JOINTS

A standard or widely-accepted fracture test of ceramic bonds is not available. Furthermore, bonds made in useful components may require special tests.

Test data should indicate the bond strength and fracture toughness relative to the joined material, thereby evaluating the quality of the bonds and quality of the bond-making process. Comparison of tests on bonds and bonded materials (including laminated material) with the same tests on monoliths will provide estimates of relative bond strength.

Both the four-point flexure test and the short bar fracture toughness test will be adapted to bond testing for this evaluation of the bonds. Flexure testing tends to test the defects on the bar surface under tension--defects that may have been introduced by the machining. Consequently, careful grinding to MIL-STD-1942, which results in controlled fine defects, would be expected to reduce variability produced by surface flaws.

A bond fracture toughness measurement will be obtained using the short bar fracture toughness test, provided the fracture occurs in the bond. The chevron-notched short bar specimen provided by the TerraTek Fractometer System has saw cuts (notches) cut in from two sides at one end leaving a chevron or V-shaped area. For a specimen with a bond, the saw cuts direct the fracture along the bond interface, when bond interface is weaker than the adjacent material as illustrated in Figure 3.

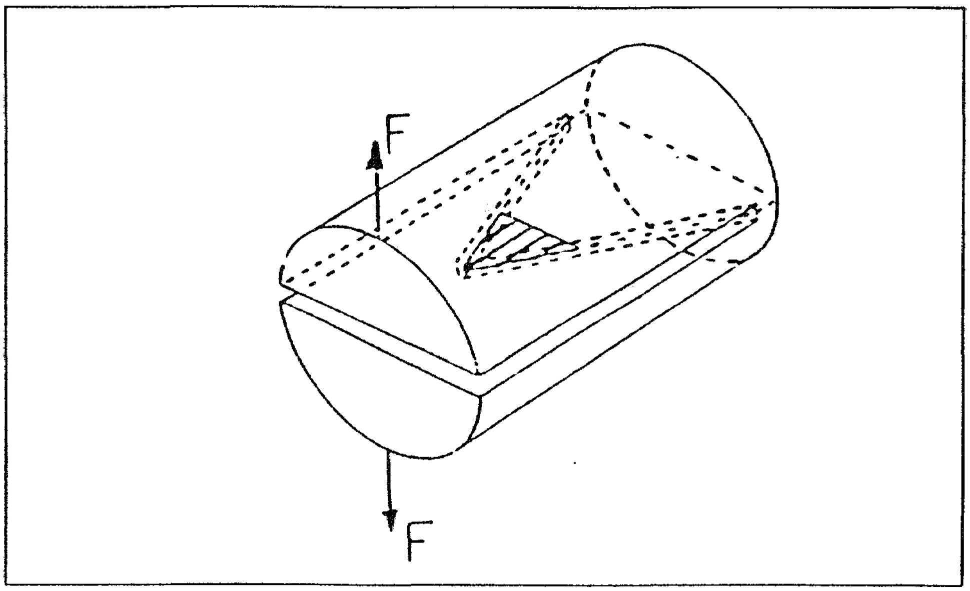


FIGURE 3 -- SHORT ROD SPECIMEN WITH JOINT INTERFACE. (THE SURFACE IS IDEALLY CENTERED AND PARALLEL TO SAW-CUT NOTCH SURFACES.)

Indentation fracture toughness tests are an alternative that is easily performed and can provide useful data on local fracture behavior for monoliths and bonded specimens.

The strength and toughness data and microscopic observations are valuable, particularly microscopic observations of large bond fracture surfaces (from short bar tests).

3.2.6 SUBTASK 2F -- DIAMETRAL COMPRESSION TEST

Diametral compression tests have potential benefit for providing tensile strength information because fractures can be initiated internally. In the flexure test, the tensile stress is maximum at the surface, so that surface defects can dominate crack initiation. Furthermore, the diametral compression test puts a large cross section under uniform tensile stress so the chance of finding large critical flaws (flaws causing failure at small stresses) is high. This cross section is on the loaded diameter of the disc or rod. The compressive load is applied to the diameter by flat platens through thin packing strips or shims that distribute the compressive stress (IBM cards are recommended). The specimen is a right circular cylinder lying on its side between two flat platens protected from the hard surfaces of the platens by shims of a softer material. The shims prevent surface damage and excessive stress concentrations.

Tensile stresses are uniform over a large area of the flat section between the diameters of the end faces normal to the platens. That is, the tensile stress is normal to the compressive stress and tends to pull the cylinder apart along this plane (as shown in Figure 4).

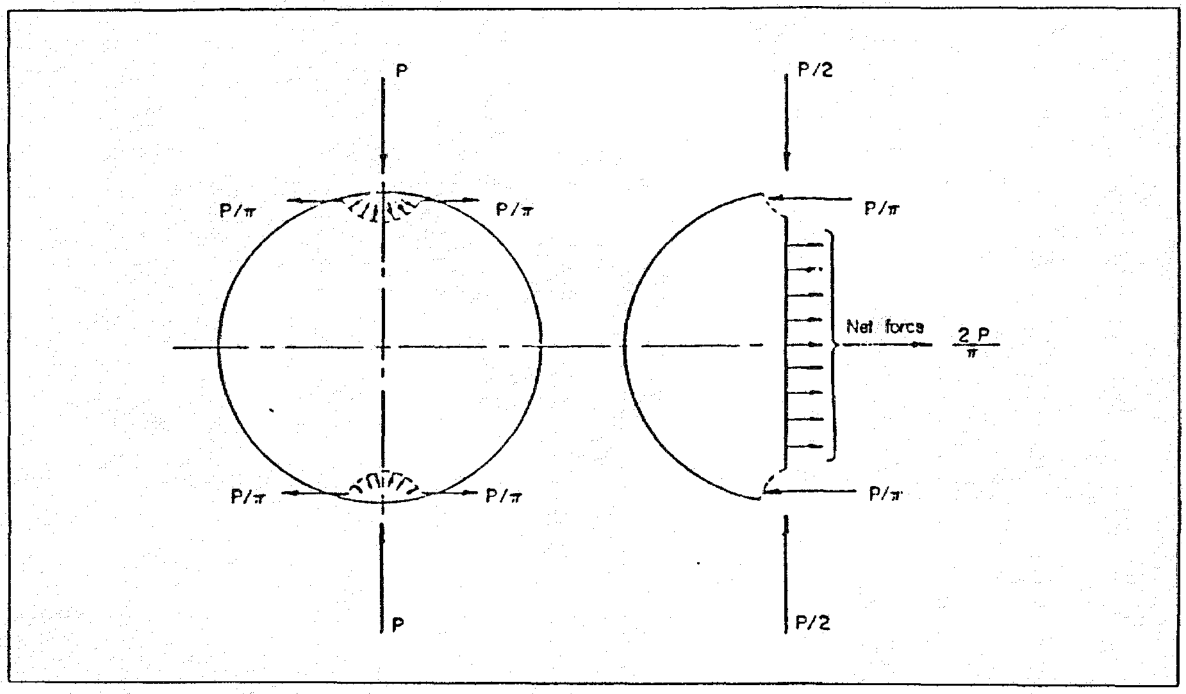


FIGURE 4 -- DEVELOPMENT OF TENSILE STRESSES THROUGH WEDGING IN A DIAMETRAL COMPRESSION SPECIMEN. IN ADDITION TO THE EXPECTED VERTICAL COMPONENT OF FORCE, THERE ARE DEVELOPED HORIZONTAL WEDGING FOR COMPONENTS OF MAGNITUDE +P/π. CONSIDERING A FREE BODY OF ONE HALF OF THE CYLINDER, THE FORCES P/π ACT AT EACH END OF THE LOADED DIAMETER, MAKING A NET HORIZONTAL FORCE OF 2P/π. THIS FORCE IS BORNE BY THE RECTANGULAR AREA FORMED BY THE INTERSECTION OF THE SPECIMEN AND A LONGITUDINAL PLANE (AREA EQUALS DIAMETER TIMES THICKNESS, DT). THUS, THE EQUATION FOR TENSILE STRESS IS OBTAINED.

Such cylindrical specimens can be core-drilled readily from ceramic pieces, which is a desirable feature of the test. If the bond can be positioned on or close to the diameters and then aligned normal to the platens, the tensile stress will be sufficiently defined for a satisfactory tensile test of the bond.

Diametral compression tests of square or rectangular cross-sectional bars are also being considered, the latter being cut from broken MOR bars.

3.2.7 SUBTASK 2G -- DEVELOPMENT OF CERAMIC SPECIMENS FOR LAMINATED BOND TESTING

The emphasis in this reporting period was on the basic procedures for formulating the binder, mixing the binder into ceramic powder, making the shapes, and browning and firing the shapes. Initially, thin plates were cut into bars of rectangular cross section. Most were cut from green (uncured) slabs, and some from brown (partially debindered) slabs. These trial bars indicated the improvements required to provide well-formed, as-fired MOR bars and plates for cutting into bars. In particular, eliminating distortion when browning large plates and eliminating distortion when cutting green material into bars require further development. Preliminary studies revealed evidence of air entrapment in the green material.

The process improvement study employed the sigma mixer (Figures 5 and 6) shortly after its delivery. The sigma blades rotate down toward the saddle in the center of the bowl, one blade rotates 40 percent faster than the other to provide the tangential mixing action desired for high viscosity mixtures.

Mixing with the sigma mixer appears to eliminate blisters and large voids from the green sheets and also appears to reduce the mixing time and labor required to obtain good quality sheets.

The plasticity and tackiness of the green ceramic sheets prevents cutting undistorted rectangular bars from the sheets. On the other hand, well-browned ceramic material was overly weakened and embrittled by binder removal, so sawing rectangular MOR bars was accompanied by substantial damage. Consequently, satisfactory as-fired MOR bars require careful curing of the green ceramic sheet to provide suitably tough ceramic sheets that can be cut without excessive distortion or fracture.

The following tasks have been identified as necessary to progress toward the contract objectives:

- Defining the process parameters required to provide sheets satisfactorily machineable into bars for browning and firing for production of MOR bars. A prebrowning limited curing is expected to stiffen and toughen the sheets sufficiently to provide the required machinability.

- Modifying process factors to decrease or eliminate warping.

- Evaluating temperature control in the sigma mixing chamber and vacuum in the chamber as a means for improving the process and the product.

- Evaluating thermoplastic compaction (warm pressing) as a means for improving bonding in lamination to eliminate lamination defects.

3.3 Task 3 -- Ceramic Fabrication and Manufacturing

Thus far, the principal activity of this task is fabricating a planar solid oxide fuel cell model. This planar oxide fuel cell subtask has gone well and is on schedule. Some effort has been devoted to participation in design activities for Subtasks 1A and 1B of Task 1.

3.3.1 SUBTASK 3A -- SOLID OXIDE FUEL CELL

In the planar solid oxide fuel cell (SOFC) design that CBSi is using, the fuel cell is divided into major structural groups. The groups consist of three primary components, namely:

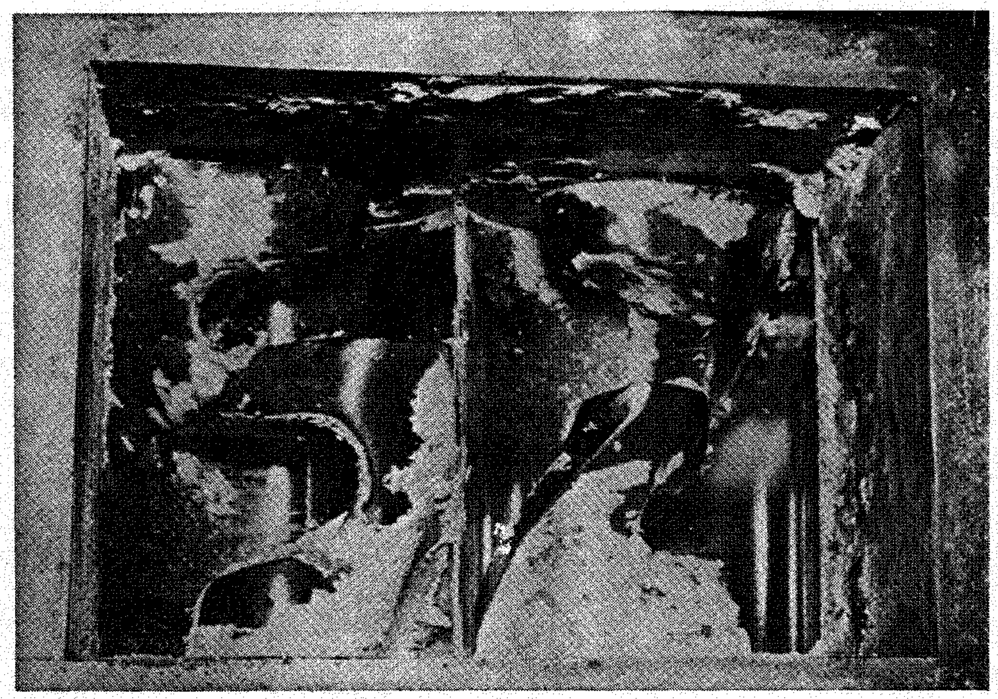


FIGURE 5 -- TANGENTIAL SIGMA BLADES IN TWO-QUART BOWL WITH MIX RESIDUE.

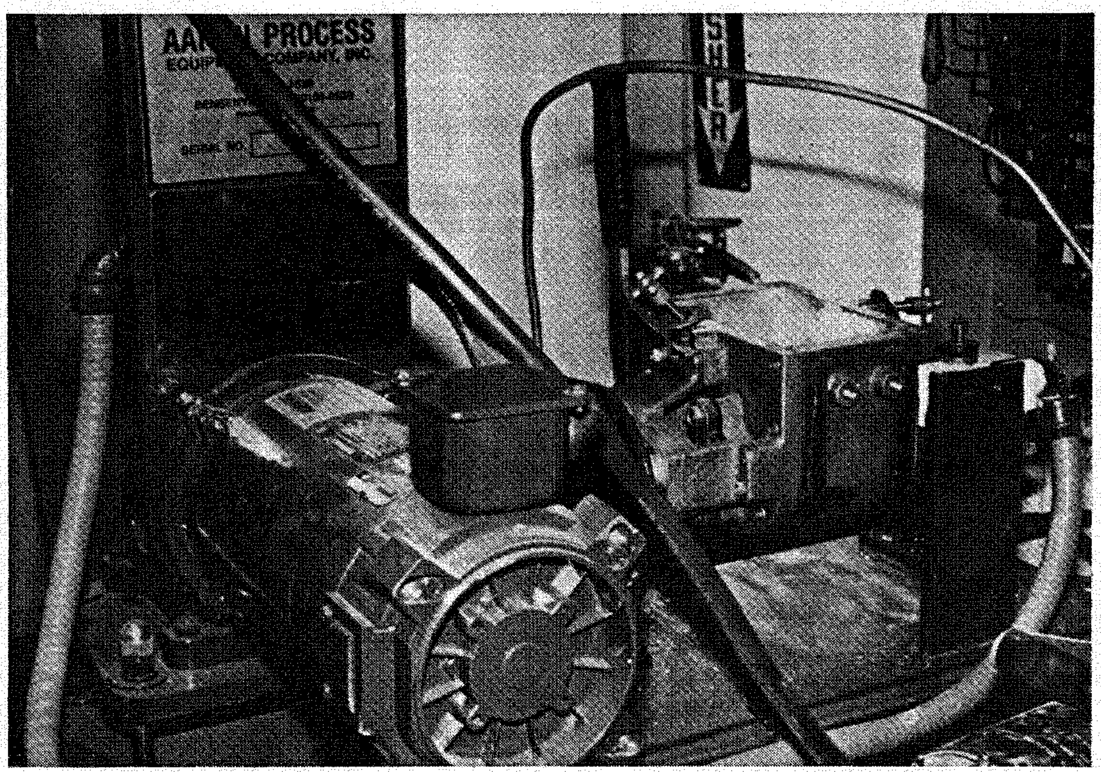


FIGURE 6 -- SIGMA MIXER WITH UNCOVERED BOWL TO THE RIGHT.

- separator plate,
- membrane, and
- spacers.

In an operating fuel cell, unlike this model, the membrane is made of three material layers instead of the single material in this cell. In addition, an operating fuel cell requires interconnector material, which will then add a fourth component; however, this component is not a structural component and may be printed on existing structural components.

In the planar SOFC being modeled, two distinct gas flow paths exist. In one path, the gas flow is critically contained within the fuel cell. In the other, the gas flow path surrounds the outside of the cell, and the flow is externally controlled. A schematic drawing of the cell is shown in Figure 7. Two different channels are shown in this drawing: the closed channels and the open channels. The open channels are open to the vertical tubes on both sides of the schematic. Since this is a cross-sectional drawing, the side tubes and the open channels that open into them are actually the closed flow channels in the fuel cell model. The channels that appear closed in the cross-sectional drawing are external to the fuel cell and are actually external flow paths.

Extending the drawing of Figure 7 into a ceramic component yields a highly complex ceramic component. However, this complex ceramic has only three components; the same components as the conceptual fuel cell model: separator plates, membranes, and spacers.

In the fuel cell model being constructed, the separator plates and the membranes are manufactured separately using different construction techniques. Individual cells are then formed by placing two membranes on each separator plate, as shown in Figure 8.

Once the individual cells are formed, these cells are joined together using spacers, as shown in Figure 9. In this final assembly, the fuel cell consists of two components, the individual cells formed with separator plates and membranes and the spacers, which are manufactured using the same technique used to fabricate the separator plate. The work outline will follow the design of the fuel cell. First, techniques will be developed that can be used to fabricate the separator plate. While these techniques are being developed, the membrane will also be developed. The second step in the plan is to join the membrane and the separator plate as visualized in Figure 8. The final step in the proposed work will be to join the individual cells, forming a full fuel cell model as seen in Figure 9.

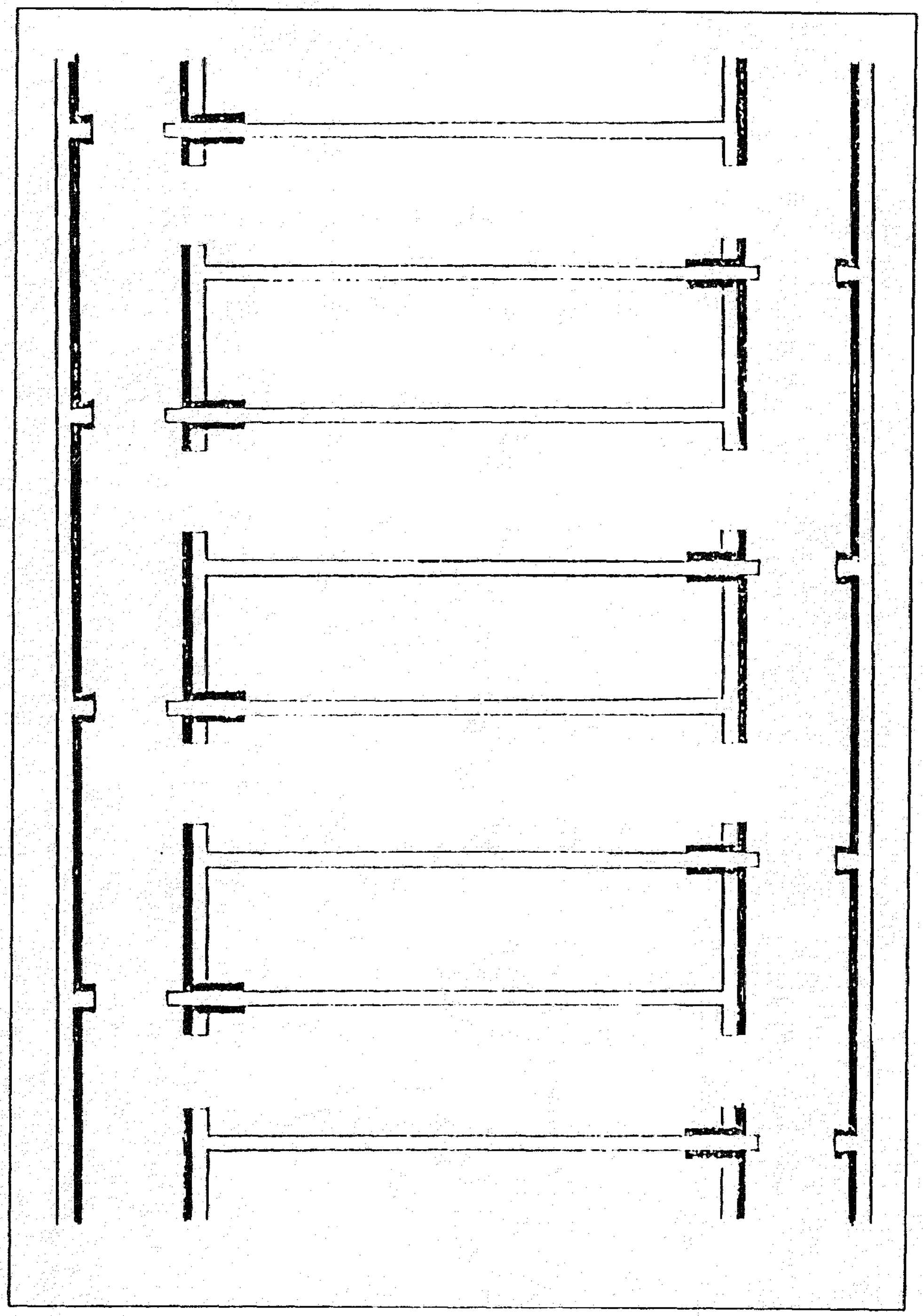


FIGURE 7 -- CROSS-SECTIONAL VIEW OF A SCHEMATIC MODEL PLANAR SOLID OXIDE FUEL CELL.

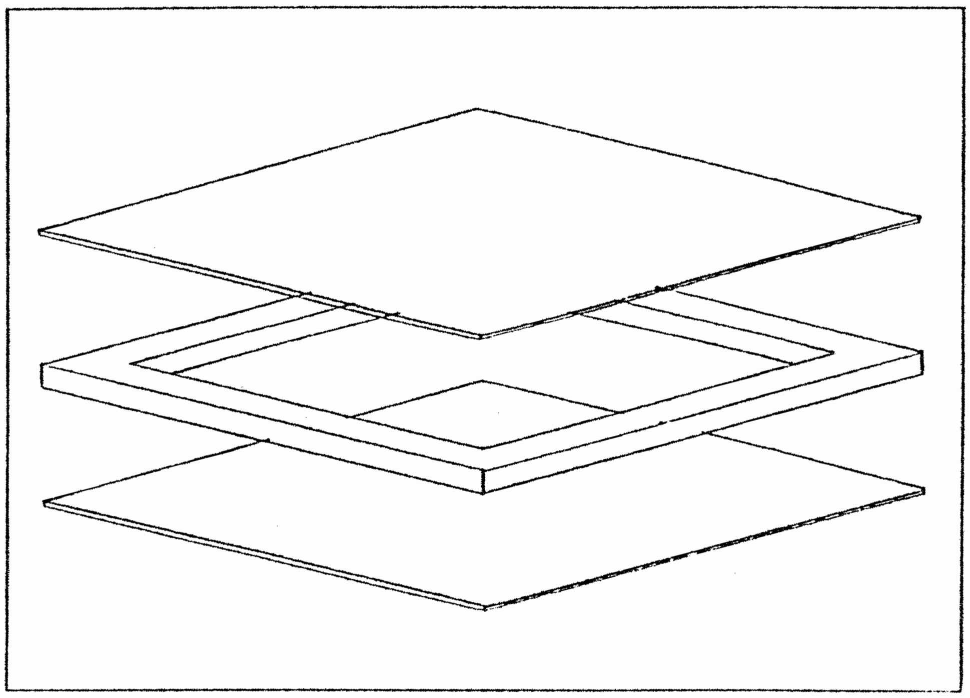


FIGURE 8 -- TWO MEMBRANE COMPONENTS JOINED WITH A SEPARATOR PLATE.

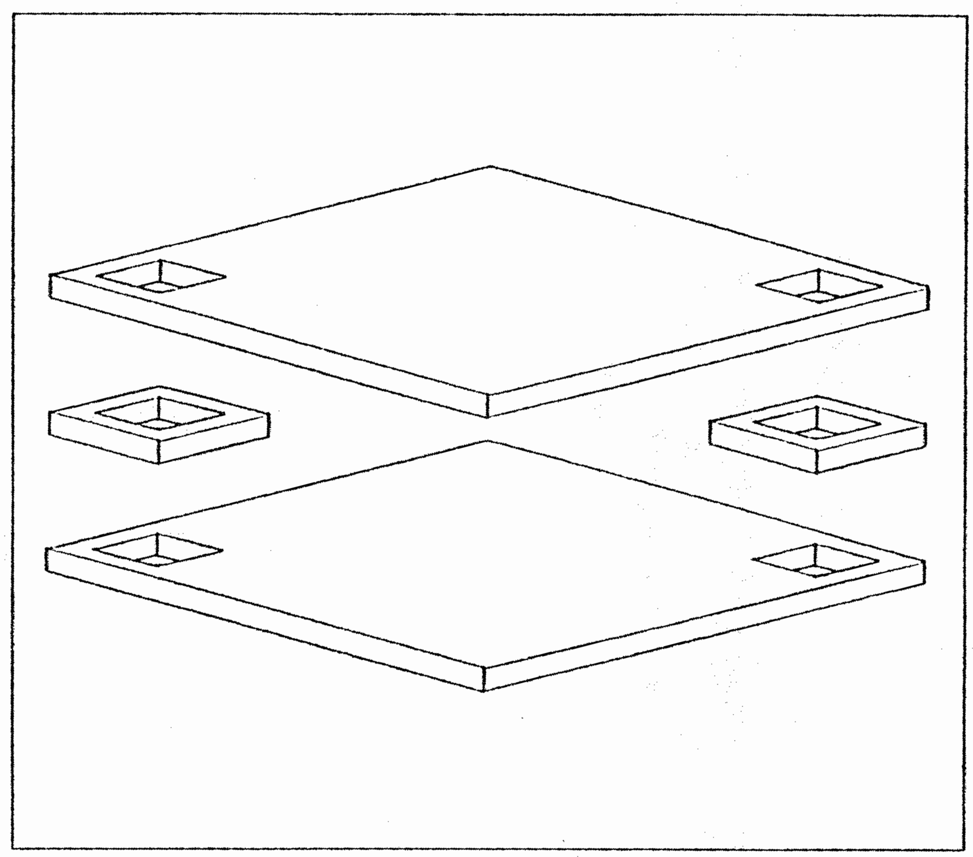


FIGURE 9 -- INDIVIDUAL CELLS JOINED TO FORM AN EXTENDED FUEL CELL.

During this quarter, CBSi worked on three different aspects of the SOFC:

- ***Membrane Separator Development***: The model SOFC being constructed has a planar design consisting of a series of parallel sheets. Individually, the sheets of our model have three laminar components. Of these three layers, two are membranes and the other is the membrane separator. The separator plate has two primary functions: to provide structural support for the cell and to direct the internal gas flow paths.

  During this quarter, the major work efforts were directed toward the separator design and maintaining flatness during processing. Although the plates still are not perfectly flat, substantial progress toward flat plates has been made.

  During the first part of this quarter, alumina was used to develop the techniques needed to produce large (4 in. by 4 in.) flat plates with internal gas passages. Since relative flatness has been achieved, we are now using zirconia materials in the separator.

- ***Membrane Development***: The goal of the membrane development is to develop the thinnest material that will still remain impermeable to hydrogen gas. Earlier in the quarter, CBSi investigated two different ways of making membranes and investigated flat plate membranes and textured membranes. Later in this quarter, the work on the textured membranes was discontinued.

  CBSi investigated tape casting and tape spraying to develop the thin zirconia membranes. Both of these techniques have produced thin membranes that can be bonded to the separator materials. CBSi is leaning toward the tape casting method, since better bonding has been achieved with tape casting materials than with sprayed materials.

  As discussed earlier, CBSi began to investigate textured membranes and flat membranes. The advantage of the flat membranes is that they are easier to produce than a textured membrane. However, the textured membranes have greater rigidity, strength, and a higher surface area.

  Two different fabrication methods were investigated in the development of textured membranes. In the first method, ceramic/binder compositions were sprayed into textured surfaces. In the second method, flat sheets were stamped with the textured pattern. Currently, neither of these two methods has definite advantages over the other.

- ***Fuel Cell Integration***: The fuel cell integration is the general assembly procedure of joining the separator to the membrane, as seen in Figure 8. As discussed, the membrane will be on both surfaces of the separator.

Later in the project, these individual cells (separator with two membranes) will be joined together to form a complex integrated assembly.

Since CBSi had yet to produce the separator or the membrane at the beginning of July, the integrating effort could not progress until both the separator work and the membrane work had matured. As expected, the integrating effort is the most difficult of the three areas discussed in this report.

Bonding the membrane to the separator has progressed well; however, we have not produced structurally sound integrated cells. The textured membranes tend to crack during thermal processing; whereas, the flat membranes sag during thermal processing and crack at the border between the separator and the membrane.

Numerous techniques have been investigated to eliminate membrane sagging prior to binder burnout. Membranes tend to remain intact during firing if they are intact during binder burnout. These techniques include placing internal flow channels in the separator plates. An example of this technique is shown in an alumina separator plate shown in Figure 10.

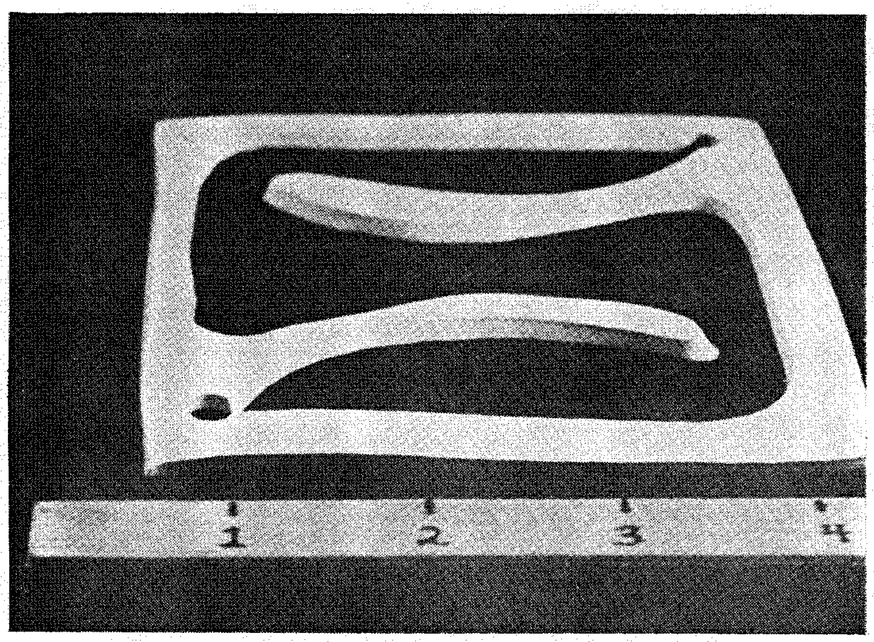


FIGURE 10 -- ALUMINA SEPARATOR PLATE.

The final technique used to eliminate membrane sagging is to place fill materials in the cavity to support the membrane during binder burnout. Although most fill material investigations have been exercises in frustration, one example of a usable fill material is shown in Figure 11. In this figure, a good cavity has been created by using a wool felt material as a fill material. Although, the wool felt material works well during a binder burnout cycle, the effect of felt degradation on the final ceramic is presently unknown.

3.3.2 SUBTASK 3B -- MHD ELECTRODE FABRICATION

No activity was planned for this subtask in this quarter. Activity will begin when the work under Subtask 1A has progressed sufficiently.

3.3.3 SUBTASK 3C -- HIGH STRESS COMPONENT FABRICATION

No activity was planned for this subtask in this quarter. Activity will begin when the component has been identified and defined and some modeling and analysis has been carried out.

4.0 PLANNED ACTIVITIES

4.1 Task 1 -- Ceramic Component Design and Analysis

4.1.1 SUBTASK 1A -- MHD ELECTRODE DESIGN AND ANALYSIS

Adequate modeling studies cannot be done unless the selected ceramic electrode material properties can be stated. Efforts will be directed toward establishing the electrode geometry, toward locating pertinent material properties, and toward establishing procedures to estimate those properties not available.

Once temperature gradients are estimated, stress gradients can be estimated, and this will lead to reevaluating geometry and materials. This iterative procedure will proceed until a design feasible for fabrication via the CCF process and practical from the MHD standpoint is produced.

Software and hardware upgrades are planned to facilitate hard copy output modeling and analysis calculations. Nonlinear property variations will be considered.

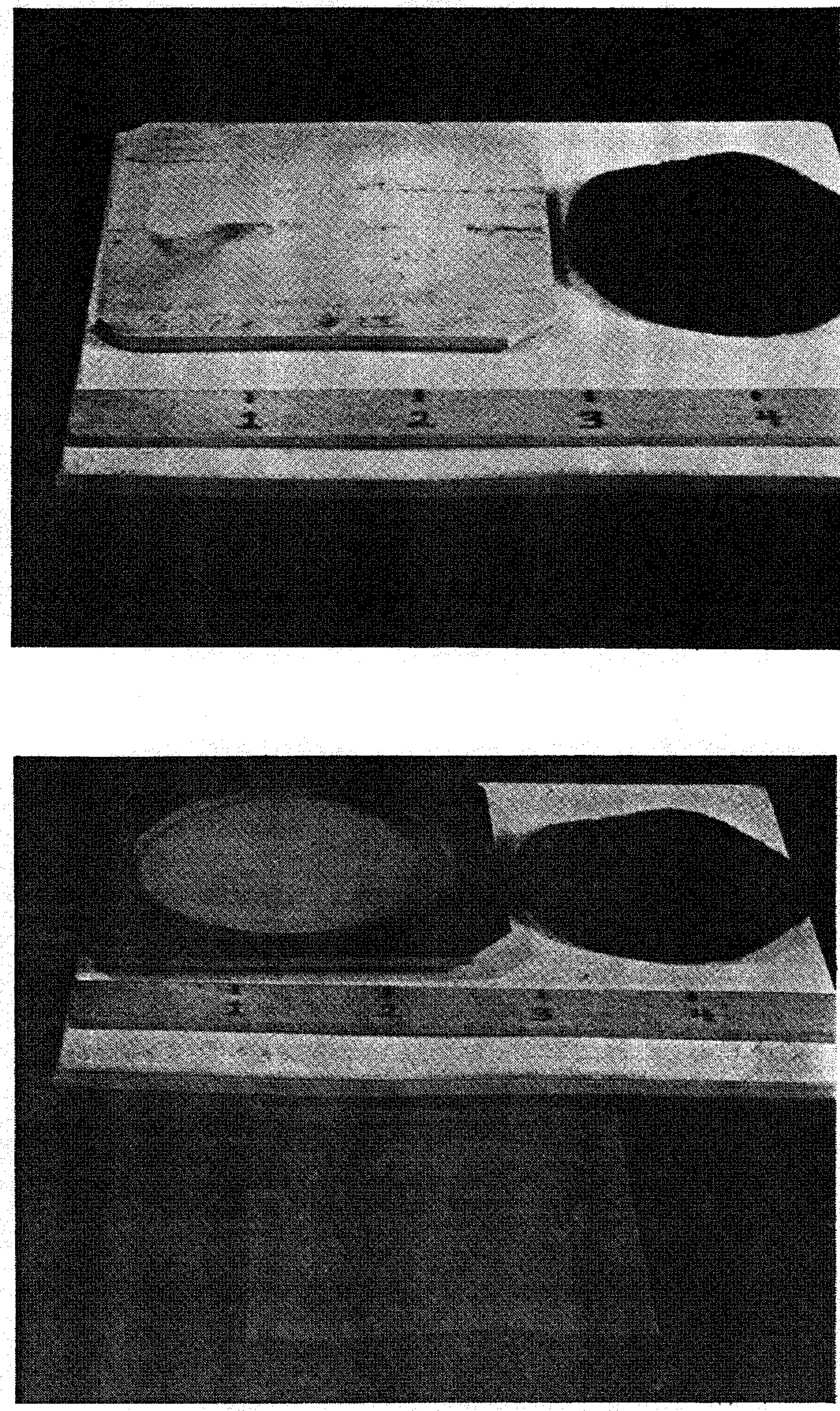


FIGURE 11 -- HALF OF AN INDIVIDUAL CELL FORMED USING A WOOL FELT FILL MATERIAL. (THE TOP PHOTO SHOWS THE MEMBRANE ON THE TOP OF THE SEPARATOR PLATE. IN THE BOTTOM PHOTO, THE HALF CELL HAS BEEN FLIPPED OVER.)

4.1.2 SUBTASK 1B -- HIGH STRESS COMPONENT DESIGN AND ANALYSIS

Exploration of the various options for a high stress component will continue with a goal of identifying the component early. Attention will be on heat exchanger applications, but ceramic armor and other possibilities will not be overlooked. The high stress component will be defined during the next quarter.

4.2 Task 2 -- Exploratory Development Using the CCF Process

4.2.1 SUBTASK 2A -- CHARACTERIZATION OF STARTING MATERIALS

No significant activity is planned for the next quarter. The current material, alumina, has been adequately characterized. If additional materials such as zirconia or other ceramic powder are obtained, more activity will occur.

4.2.2 SUBTASK 2B -- MECHANICAL TEST METHODS

This subtask is essentially completed. Test methods have been reviewed. No further activity is planned.

4.2.3 SUBTASK 2C -- FLEXURAL TESTING TO MIL-STD-1942

Testing will be carried out as specimens become available (Subtask 2G). Determination of a vendor for elevated temperature MIL-STD-1942 flexure testing is planned. A vendor for machining test bars to MIL-STD-1942 will be selected.

4.2.4 SUBTASK 2D -- SHORT ROD FRACTURE TOUGHNESS TESTING

Plans are to refurbish the available TerraTek Fractometer instrument and to send a professional to TerraTek for training. Actual testing will take place only when specimens become available.

4.2.5 SUBTASK 2E -- FRACTURE TESTING OF BONDS

No planned activity for this subtask during the next quarter.

4.2.6 SUBTASK 2F -- DIAMETRAL COMPRESSION TEST

No planned activity for this subtask during the next quarter.

4.2.7 SUBTASK 2G -- DEVELOPMENT OF CERAMIC SPECIMENS FOR LAMINATED BOND TESTING

Most activity next quarter will be concentrated on this subtask. Shape control problems have to be explored and solved so satisfactory shapes for test bar fabrication can be reliably produced.

4.3 Task 3 -- Ceramic Fabrication and Manufacturing

4.3.1 SUBTASK 3A -- SOLID OXIDE FUEL CELL

Integrating the joined cell membrane and separator of individual cells to form a full fuel cell will be the principal focus of work during the next quarter.

4.3.2 SUBTASK 3B -- MHD ELECTRODE FABRICATION

Work on MHD electrode fabrication will begin when the design phase of Task 1 has advanced sufficiently, probably toward end of the quarter.

4.3.3 SUBTASK 3C -- HIGH STRESS COMPONENT FABRICATION

No fabrication activity is planned for the next quarter.

5.0 TECHNICAL SUMMARY

Three tasks have been set up. Task 1, assigned to MSE, Inc., deals with design and modeling analysis of a ceramic electrode for an MHD generator with SDI applications and of a ceramic component that sees a high stress, either mechanical or thermal in origin, in service. Task 2, subcontracted to Applied Technology Laboratories (ATL), deals with developing test data, principally modulus-of-rupture (flexure, 4-point bending) data, at ambient and at elevated temperatures to 1,000 °C. The data will compare monolithic and bonded (laminated) ceramic specimens prepared using the CCF process. Task 3, subcontracted to Ceramic Binder Systems, Inc. (CBSi), involves fabricating three different ceramic items with defense applications using the CCF process to demonstrate the versatility and applicability of the CCF process. The items are a model planar solid oxide fuel cell assembly, the MHD electrode designed in Task 1, and the high stress ceramic component also designed in Task 1.

5.1 Task 1 -- Ceramic Component Design and Analysis

Initial effort in this task was to explore the feasibility of designing an MHD electrode with integral electronic functions such as a switching capability and the ability to function with a hot-face temperature of approximately 2,000 °C. It was concluded that this was not feasible within the project time frame due to the current carrying limitations of the feasible ceramic compounds considered. Attention has since focused on a hot ceramic electrode fabricated from graded, laminated, ceramic composite layers to the rear of which electronic components might be attached. Some very preliminary modeling has been done, but property values are difficult to locate and are delaying progress to some degree.

5.2 Task 2 -- Exploratory Development Using the CCF Process

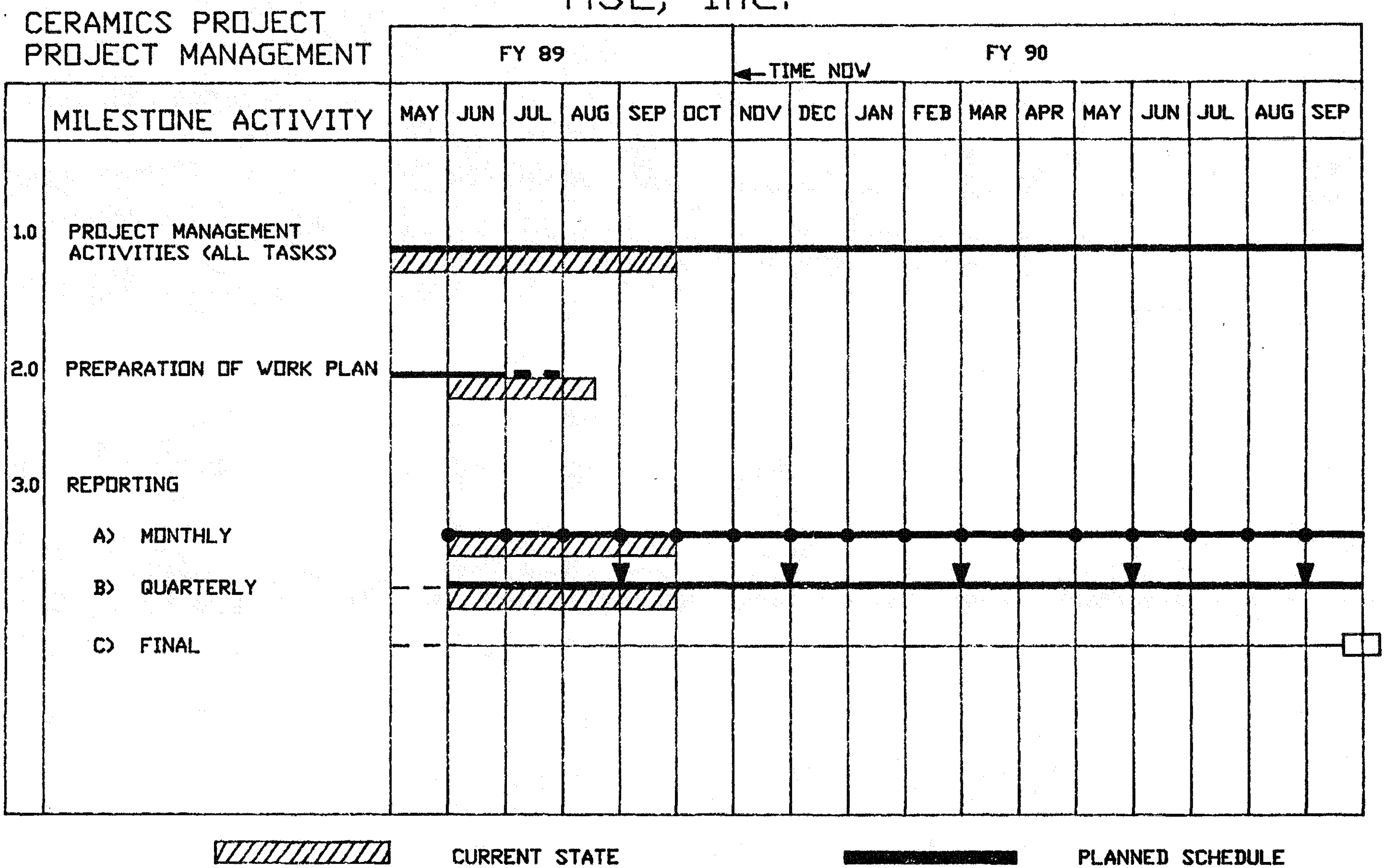
The first step in this task was to transfer CCF process technology from CBSi to ATL personnel. Numerous initial activities included selection, procurement, and characterization of starting materials. Progress was slow due to the need for laboratory renovations and the procurement of some major equipment items. A review of available mechanical test methods was accomplished. Four-point bend tests will be conducted to give modulus-of-rupture values according to MIL-STD-1942 at room ambient and at 1,000 °C. Some short-rod fracture toughness tests will be carried out, and some use of diametral compression tests is anticipated. Owing to difficulties in producing browned (partially debindered) shapes free from defects such as warping and blistering, adequate test specimens have not yet been produced. The project is behind schedule in spending as well as in technical progress. All efforts in the next quarter will be focused on solving the problem of shape control.

5.3 Task 3 -- Ceramic Fabrication and Manufacturing

Task 3 was able to progress immediately because a design for the planar solid oxide fuel cell existed as did laboratory facilities and manpower. Little additional staff was required, and work to produce the thin ceramic membranes by tape casting was quickly initiated. Cell separators were also fabricated, and procedures to bond them to membranes were also initiated during the quarter. Other accomplishments were technology transfer of the CCF process to ATL staff and participation in the Task I design group studies. This task is on schedule.

APPENDIX A -- Project Schedule

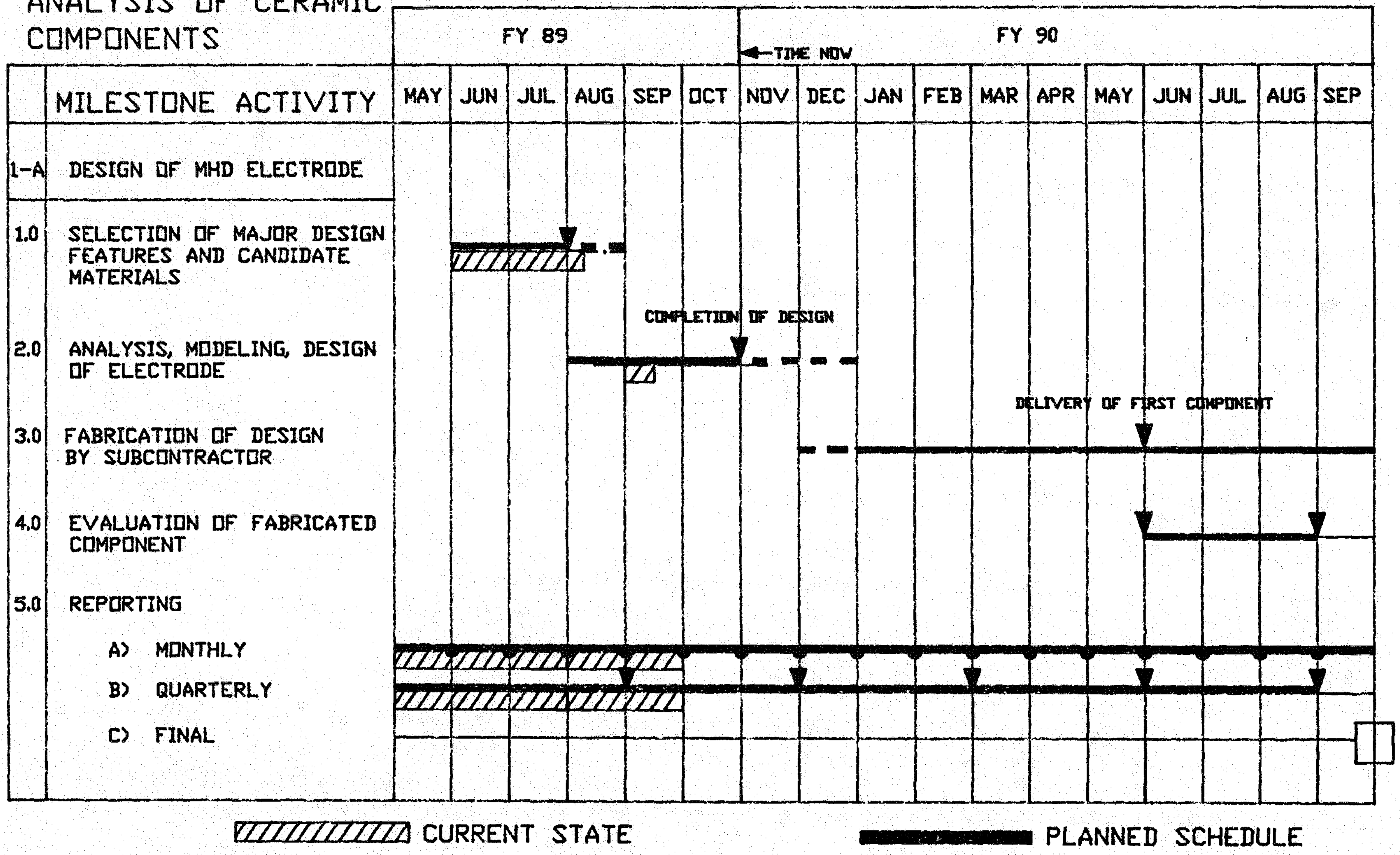
MSE, Inc.



CERAMICS PROJECT
PROJECT MANAGEMENT
FY 89
FY 90
TIME NOW
MILESTONE ACTIVITY
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
1.0 PROJECT MANAGEMENT ACTIVITIES (ALL TASKS)
2.0 PREPARATION OF WORK PLAN
3.0 REPORTING
A) MONTHLY
B) QUARTERLY
C) FINAL
CURRENT STATE
PLANNED SCHEDULE

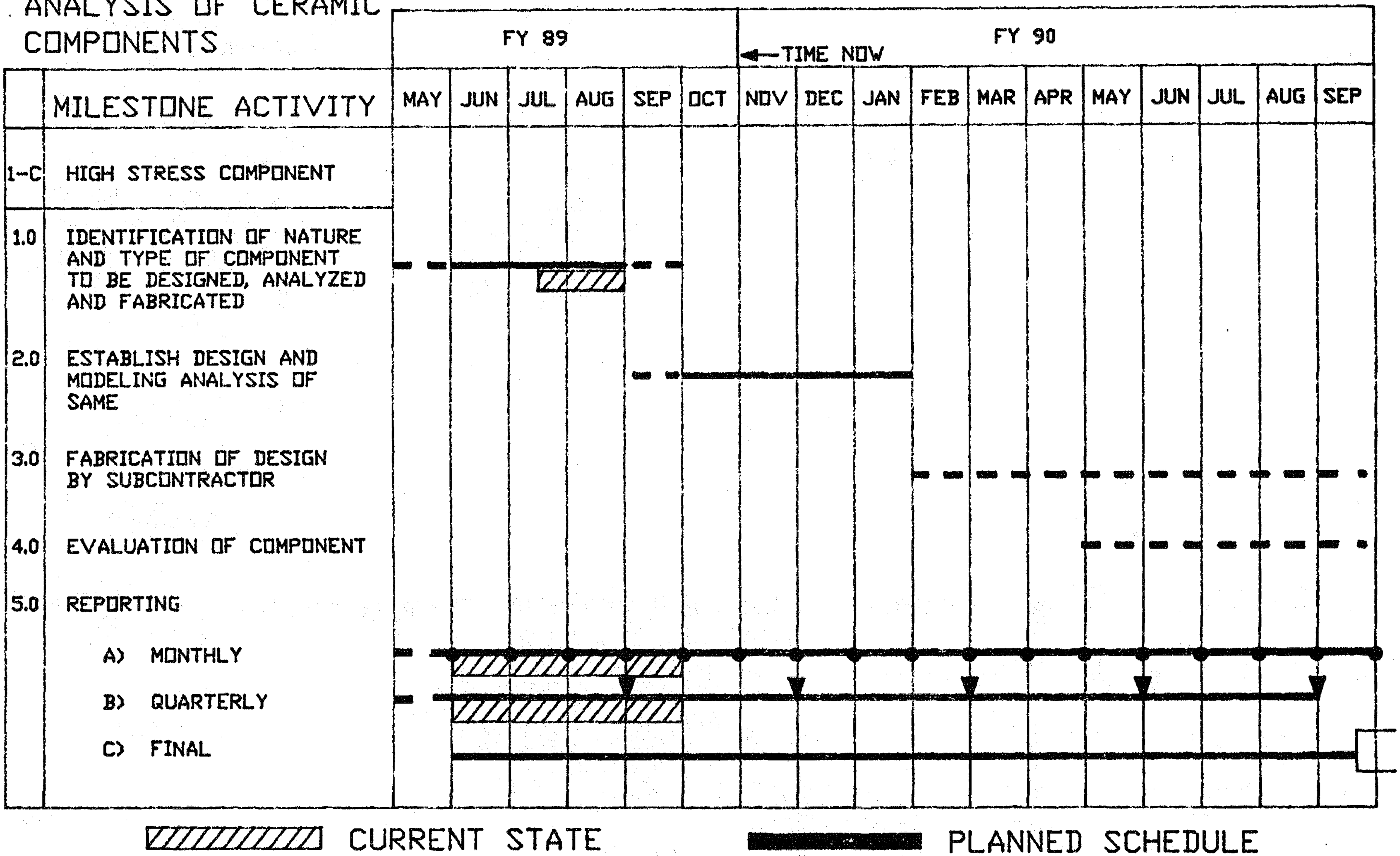
TASK I - DESIGN AND ANALYSIS OF CERAMIC COMPONENTS

MSE, Inc.



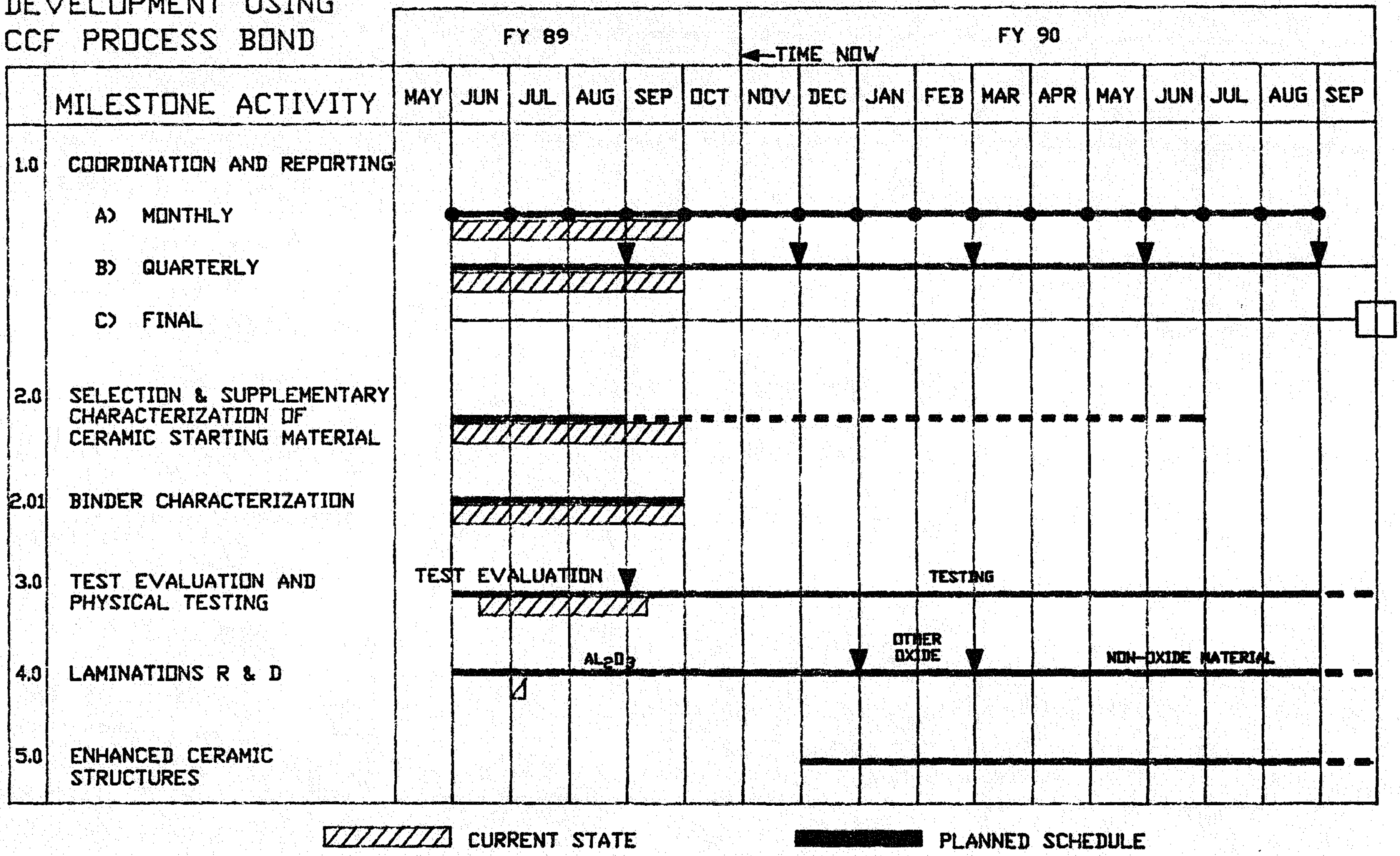
TASK 1 - DESIGN AND ANALYSIS OF CERAMIC COMPONENTS

MSE, Inc.



MONTANA TECHNOLOGY COMPANIES, INC.
APPLIED TECHNOLOGY LABORATORIES

TASK II - EXPLORATORY DEVELOPMENT USING CCF PROCESS BOND



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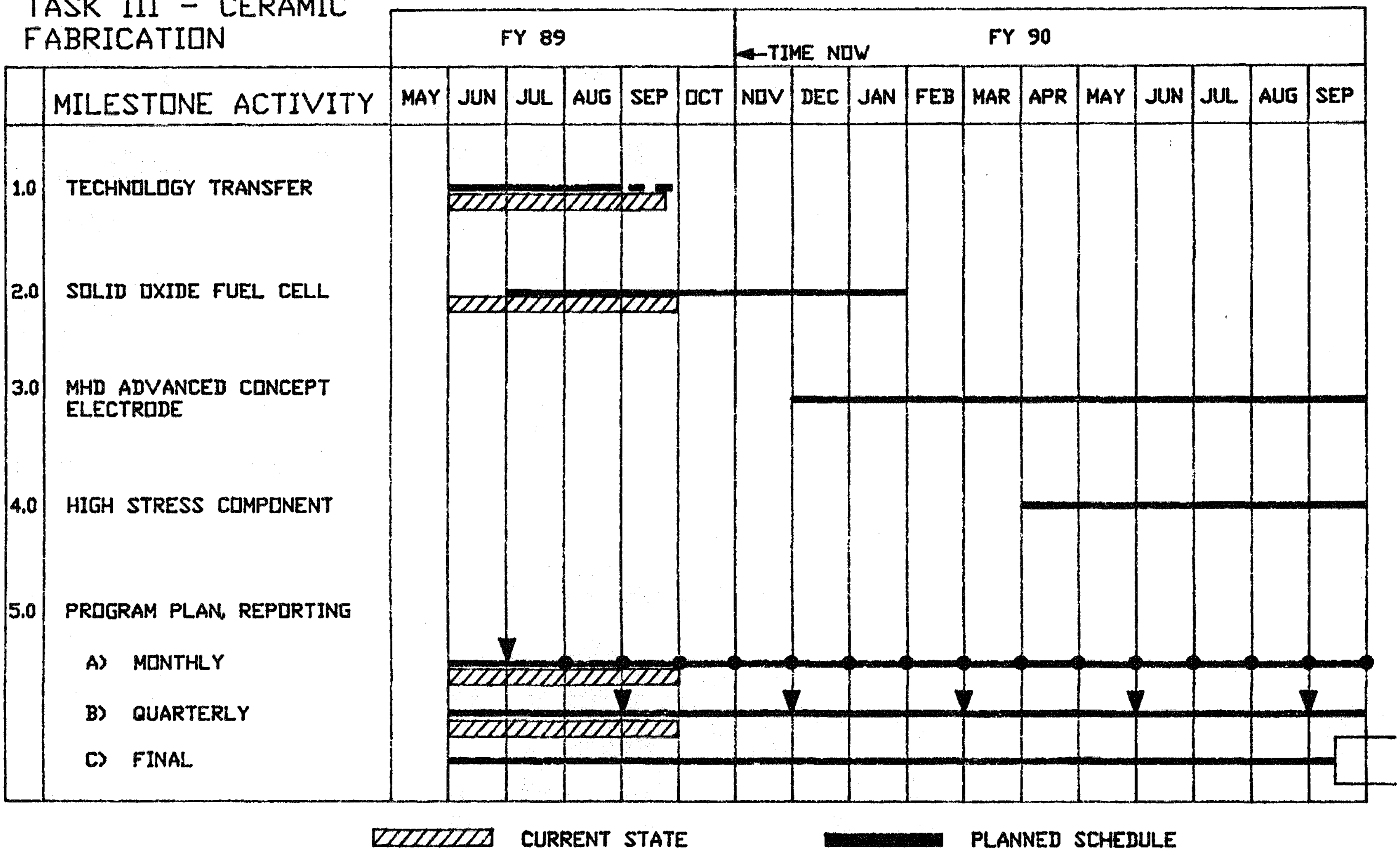
CERAMIC BINDER SYSTEMS, INC

TASK III - CERAMIC FABRICATION



APPENDIX B -- Discussion of MHD Electrode Considerations

One proposed approach was the design and fabrication of an advanced MHD electrode having integral electronic functions, meaning that built into the body of the electrode would be layers having n-type and/or p-type conductive properties such that the electrode could be switched from a high to a low conductive state and vice-versa. This is an attractive idea that might well simplify and facilitate power conditioning and arc control in MHD generators. Another proposed approach was that a ceramic electrode having integral cooling passages could be designed and fabricated. In turn, this leads to the concept of fabricating integral wall segments where insulators and electrodes are monolithic, containing built-in cooling passages.

In fact, several other advanced concepts, all utilizing the capabilities of the CCF process were outlined in a proposal[5] submitted in 1982 to the MHD Division of DOE by Applied Technology Laboratories. The literature also describes many other efforts to develop hot ceramic electrodes for MHD generators. Papers by P. J. Tilborg and J. H. N. Verheugen[6], J. Dong-liang, et al.[7], J. W. Hafstrom and J. T. Dusek[8], D. D. Marchant and J. L. Bates[9], and W. R. Cannon, et al.[10] are cited as typical of many efforts to develop hot ceramic electrodes.

For the most part, the objective of these investigations was to develop an electrode for service in a ground-based electric utility-type generator. Similarly, coal-fired slagging generators were the objective of the electrode development. This meant that electrode current densities on the order of 10^4 amp/m^2 were involved and that electrode lifetimes substantially in excess of 10^3 hr. were targeted. The latter requirement means that electronic conductivity is required in the electrode throughout the temperature gradient from the hot side to the cooler rear side where electrical current leadouts are provided. Any degree of ionic conductivity can lead to problems. For example, the discharge of oxygen anions can lead to oxygen bubble formation generating pressures leading to spalling of the electrode. In addition, intense oxidation reactions can occur at the anode current leadout leading to failures. Very complex interactions and reactions can occur if slag is present to react with the discharged anions or cations from either the slag or the electrode materials.

The use of metallic electrodes avoids ionic conductivity in the electrode but ionic effects still occur at the electrode-slag interface. Few metals have the potential to serve reasonably well at the temperatures prevailing at the slag/electrode or the plasma/electrode interface. Ceramic materials offer strength and stability advantages so a variety of ceramic compositions that exhibit substantial electronic conductivity have been investigated as noted above. These include materials such as lanthanum chromite and other related materials such as lanthanum strontium ferrite as well as ceria-doped zirconia and ceria-yttria-hafnia and other relatively exotic compositions.

Essentially all of these compositions behave as degenerate semiconductors and none appear to have 100 percent electronic conductivity. Bates[11] reports a hafnia-praseodymium oxide-indium oxide composition which showed less than 0.2 percent ionic conduction so materials with approximately 0.1 percent ionic conduction are feasible. However, even this low ionic contribution can be excessive. Moreover, even these highly electronic ceramic materials exhibit conductivities an order of magnitude or so less than those of metallic materials so that one may anticipate that these materials, when doped at a level to produce extrinsic n- or p-type semiconductive behavior, would exhibit still lower electrical conductivities.

Another complication is that probably no single ceramic material has electrical conductivity enabling it to be used over the temperature interval prevailing between the hot plasma/electrode interface and the current leadout on the rear face of the electrode. This has been recognized by various investigators, for example Bates and Marchant.[12] Both they, as well as earlier investigators, have proposed that the electrode be constructed of two or more layers of different composition to optimize the electronic conductivity of the different layers at the different temperatures prevailing in the electrode.

From the above it is concluded that ceramic electrodes with integral electronic n- or p-type layers are not compatible with the current densities desired in MHD electrodes at the present time. There is one possible exception, ß-silicon carbide, which is reported to be fabricated into transistors capable of operation at temperatures up to 650 °C. However such devices are epitaxial, thin-film, grown structures, and their technology is not adaptable to the polycrystalline morphology inherent to the CCF process.

To design an advanced MHD electrode, some characteristics of the MHD generator itself have to be specified. The 10-MW rocket driven disk generator described by Solbes, et al.[3] is noted. However, for present purposes, it was assumed that the MHD generator would not be coal-fired and that the lifetime of the electrode could be expected to be only a small number of hours. Startup from around 0 °C was assumed, with a run time of only a few minutes; thus, thermal shock effects would be a major problem. The hot electrode face temperature would be at least 2,000 °C but less than about 2,800 °C, and the rear face temperature for current leadout would be about 300 °C. If cooling is found to be necessary, it will be provided by incorporating integral cooling passages. Current densities in the range of 10^5 amp/m^2 or higher were targeted. Lacking better knowledge of heat fluxes into the electrode, it was assumed for initial analysis purposes that heat flux of the same order as experienced in the CDIF generator would be present; this is on the order of 5×10^6 W/m^2. In fact, substantial Joule heating effects are anticipated at the current densities assumed and this complicates the design. Modeling and analysis of simple geometric electrode shapes of ceramic-metal composites has commenced. The incorporation of metal is seen as necessary to provide for electronic conduction at the required current densities throughout the desired temperature range of the electrode.

The CCF process, because of its ability to bond ceramic or metallic layers, is suited to the fabrication of complex, graded electrode structures. The design being worked out is expected to be fabricated via the assembly of various layers of variable shapes and compositions. It appears that gas cooling passages will be necessary. Thermal stresses will be a major problem and the choice of electronic conductor will be strongly influenced by the need to minimize thermal expansion differences.

APPENDIX C -- References

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