MASTER

HIGH TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

Final Technical Status Report

For the Period

1 March 1979 - 31 March 1980

Paul A. Lessing

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**The Montana Energy
and MHD Research
and Development
Institute, Inc.**

Post Office Box 3809
Butte, Montana 59701

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The Montana Energy and MHD
Research and Development Institute, Inc.
P. O. Box 3809
Butte, Montana 59701

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TABLE OF CONTENTS

I. OBJECTIVE	1
II. INTRODUCTION.	1
III. PROGRESS SUMMARY.	2
A. Task 1 - Materials Identification	2
B. Task 2 - Fiber Formation.	46
1. Process	46
2. Strength Tests.	51
IV. CONCLUSIONS	54
V. APPENDIX A	
APPENDIX B	

EXECUTIVE SUMMARY

The objective of the program has been to evaluate potential materials for their chemical and physical stability in molten carbonate fuel cell electrolyte. Eleven powdered candidate materials were selected based on previous physical and chemical stability tests at elevated temperatures on solid materials and/or their thermodynamic stability with respect to proposed degradation reactions.

The eleven candidate materials, plus gamma lithium aluminate, were characterized prior to corrosion testing utilizing a) Chemical Analysis, b) X-ray Diffraction For Phase Identification, c) Scanning Electron Microscopy (SEM), and d) Surface Area Analysis (B.E.T.). Extremely careful and detailed testing was performed in every case to provide an accurate baseline with which to compare the ceramics after corrosion testing. If detailed chemical analysis was not available from the supplier on starting materials, emission spectrochemical analysis was performed. The X-ray diffraction work was performed using unfiltered Cu radiation to increase the intensity of any minority phases present. This leads to the presence of K_{β} peaks in the patterns and for many of the ceramic compositions, complicated (many peaks) patterns result. To enhance phase identification and to use quantitative match parameters, a computer program written for the Joint Committee on Powdered Diffraction Standards (JCPDS) called the Johnson Search Match program was used.

Extensive work was performed in characterizing the powders using SEM micrographs. Results were quantified by counting up to 500 particles using random linear intercept techniques. Normally, both an agglomerate and particle size and range were determined. The morphology was also noted. An examination of SEM micrographs show that

there is a great variety in the powder agglomerates and the morphologies encountered in this study. This information was used in conjunction with the macroscopic surface area and mesh information to form a more complete characterization of the powders--both before and after corrosion testing.

The powders were corrosion tested initially for 200 hours by heating to 700°C in a mixture of 62% Li_2CO_3 - 38% K_2CO_3 under a fuel gas atmosphere. The gas composition was based on reformed Naptha at 700°C and consisted of 50.2% H_2 , 10.8% CO , 9.5% CO_2 , and 29.5% H_2O . The samples were tested in an inert container made by coating the interior of alumina crucibles with a layer of 0.002-inch gold.

Seven of the original test materials (Al rich MgAl_2O_4 , Mg rich MgAl_2O_4 , $\text{Al}_2(1-x)\text{Cr}_2x\text{O}_3$, CaZrO_3 , MgTa_2O_6 , CoAl_2O_4 , and MgZrO_3) were eliminated from further testing after completion of the 200-hour test. These materials showed one or all of the following instabilities: phase changes, substantial particle growth, changes in particle morphology, and/or high solubility in the electrolyte. Li_2ZrO_3 was a common degradation product of the reactions and may be a reasonable material for use in molten carbonate fuel cells. The remaining materials (ZrO_2 stabilized with CaO , ZrO_2 stabilized with Y_2O_3 and Cr_2O_3 , Y_2O_3 . Al_2O_3 , $\gamma\text{-LiAlO}_2$, ThO_2 , and CeO_2 as a potential substitute for ThO_2) were corrosion tested for 1000 hours under the same conditions as the previous 200-hour test.

The CaO stabilized ZrO_2 had a reasonably small increase in mean particle size from $2.3 \pm 4.0 \mu\text{m}$ but appeared to be slowly changing its phase while losing calcium to the carbonate. The $\gamma\text{-LiAlO}_2$ particles increased from a $0.10 \mu\text{m}$ to $0.40 \mu\text{m}$ mean particle size after

1000 hours including the formation of some large (up to 10 μm) bi-pyramids. There was a possible loss of the small amount of $\alpha\text{-LiAlO}_2$ present in the sample before testing. The particle growth was accompanied by a significant amount of Al in the melt. The $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ looked very good at 200 hours, and the chemical leaching was good for 1000 hours, but between 200 and 1000 hours, there was rapid particle growth ($5.0 \rightarrow 40 \mu\text{m}$) with some changes occurring in the X-ray pattern. The ThO_2 exhibited initial particle growth from 0 to 200 hours but appeared stable between 200 and 1000 hours with a mean particle size of 4.0 μm with little solubility and no phase change. Similarly, the CeO_2 had no phase change but showed substantial solubility and particle growth ($2.0 \rightarrow 5.0 \mu\text{m}$). The ZrO_2 stabilized with Y_2O_3 and Cr_2O_3 had low solubility, little particle growth ($4.0 \rightarrow 5.0 \mu\text{m}$), and unchanged X-ray pattern. It must be pointed out that the fully stabilized ZrO_2 (doped with Y_2O_3 and Cr_2O_3) had a much larger mean particle size than the $\gamma\text{-LiAlO}_2$ (4.0 versus 0.1 μm), but the stabilized ZrO_2 had a larger surface area (10 m^2/g versus 5.51 - 6.61 m^2/g) than the $\gamma\text{-LiAlO}_2$.

Powders of ZrO_2 stabilized with Y_2O_3 and Cr_2O_3 , ThO_2 , and $\gamma\text{-LiAlO}_2$ show the most corrosion resistance to 62% Li_2CO_3 -38% K_2CO_3 at 700°C under a reformed Naptha fuel gas atmosphere for 1000 hours. Other compositions studied may have acceptable corrosion resistance if in a dense monolithic form. Lithium zirconate (Li_2ZrO_3) appears to be a stable corrosion product, and its use should be investigated further.

LIST OF TABLES

	Page
Table I. Properties of Candidate Materials Prior to Testing	4
Table II. Particle Size	10
Table III. X-ray Phase Identification (Powders)	12
Table IV. Chemical Analysis of Filtered Carbonate (After 200-hour Tests)	14
Table V. Compilation of Evaluations (After 200-hour Tests)	16
Table VI. Particle Size	17
Table VII. X-ray Phase Identification (Powders)	18
Table VIII. Chemical Analysis of Filtered Carbonate (After 1000-hour Tests)	19
Table IX. Compilation of Evaluations after 1000-hours	36

LIST OF FIGURES

	<u>Page</u>
Figure 1a. Prior Testing γ -LiAlO ₂	21
Figure 1b. Post 1000-hr. corrosion test γ -LiAlO ₂	21
Figure 2a. Post 1000-hr. corrosion test γ -LiAlO ₂	22
Figure 2b. Post 1000-hr. corrosion test γ -LiAlO ₂	22
Figure 3. Post 1000-hr. corrosion test γ -LiAlO ₂	23
Figure 4a. γ -LiAlO ₂ fibers fired to 1350°C	23
Figure 4b. γ -LiAlO ₂ fibers fired to 1350°C	24
Figure 5. γ -LiAlO ₂ fibers fired to 1350°C 70° tilt dynamic focus	24
Figure 6a. γ -LiAlO ₂ fibers fired to 1350°C - fiber "mat"	25
Figure 6b. "Close-up" of γ -LiAlO ₂ fiber "mat"	25
Figure 7a. Spinel fibers after 200-hr. corrosion test	26
Figure 7b. Spinel fibers after 200-hr. corrosion test	26
Figure 8. Mean particle size of candidate materials before and after 200-and 1000-hr. corrosion tests	27
Figure 9. Mean particle size of candidate materials before and after 200-and 1000-hr. corrosion tests	28
Figure 10. Chemical analysis of cation concentrations found in leached carbonates	29
Figure 11. Chemical analysis of cation concentrations found in leached carbonates	30
Figure 12. Chemical analysis of cation concentrations found in leached carbonates	31
Figure 13a. CeO ₂ fibers before testing	37
Figure 13b. CeO ₂ fibers before testing	37
Figure 13c. CeO ₂ fibers after 1000-hr. test	38
Figure 13d. CeO ₂ fibers after 1000-hr. test	38

LIST OF FIGURES (Continued)

	<u>Page</u>
Figure 14a. γ -LiAlO ₂ fibers before testing (sintered at 1550°C)	40
Figure 14b. γ -LiAlO ₂ fibers before testing (sintered at 1550°C)	40
Figure 14c. γ -LiAlO ₂ fibers after 1000-hr. test	41
Figure 14d. γ -LiAlO ₂ before testing (sintered at 1500°C)	41
Figure 14e. γ -LiAlO ₂ after 1000-hr. test	42
Figure 14f. γ -LiAlO ₂ after 1000-hr. test	42
Figure 15a. ZrO ₂ + Y + Cr fibers before testing	43
Figure 15b. ZrO ₂ + Y + Cr fibers before testing	43
Figure 15c. ZrO ₂ + Y + Cr fibers after 1000-hr. test	44
Figure 15d. ZrO ₂ + Y + Cr fibers after 1000-hr. test	44
Figure 16. Fibers are formed by spinning slurry	47
Figure 17. Closeup view of "Green" fibers collected around perimeter of spinning apparatus	48
Figure 18a. SEM photomicrograph of Al ₂ O ₃ sintered fiber - 10,300x	50
Figure 18b. SEM Photomicrograph of Al ₂ O ₃ sintered fiber - 760x	50

HIGH-TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

I. OBJECTIVE

The objective of this program was to develop strong thin fibers of materials which are chemically and physically stable in a molten carbonate fuel cell electrolyte at 600 to 700°C and to perform the materials characterization necessary to determine the stability of the fibers in the molten carbonate electrolyte.

II. INTRODUCTION

This report describes work performed under a continuation of DOE Contract No. EC-77-C-03-1485. Work began under a precontract agreement during March 1979 and continued until March 1980. From the Statement of Work contained in the renewal contract, MERDI abstracted tasks and subtasks. The two tasks are: 1) Materials Identification and 2) Fiber Preparation. The following subtasks were identified:

- 1.1 List Candidate Materials,
- 1.2 Determine Chemical Stability of Candidate Materials,
- 1.3 Determine Physical Stability of Candidate Materials,
- 2.1 Prepare Fibers, and
- 2.2 Evaluate Fibers.

A project milestone chart was established by MERDI that showed tasks, subtasks, tests used in support of subtasks, information due in reports, and a tentative timetable. The timetable was established as a guideline for the tasks that would correspond to a completion of all tasks by March 1980. It was recognized that it might not be possible to meet the time schedule outlined in the milestone chart. However, a concerted effort was made to meet that schedule, and all work is complete

at this time, 15 April 1980. Copies of the MERDI milestone charts are included with this report as Appendix A. As tasks were accomplished, the horizontal bars were filled in to illustrate progress. Funds were completely expended as of 13 March 1980, and parts of Subtask 2.2 and the writing of this report were funded by MERDI.

It was found during the course of the experiments that Atomic Absorption (AA) and X-ray diffraction tests would yield no additional information about the 1000-hour fiber corrosion experiments, and these tests were eliminated from the original schedule.

III. PROGRESS SUMMARY

A. Task 1 - Materials Identification

A list of ceramic materials which were potentially stable in molten carbonates was established, namely;

- 1) Al rich MgAl_2O_4 ,
- 2) ThO_2 ,
- 3) ZrO_2 stabilized with Y+Cr,
- 4) ZrO_2 stabilized with Ca,
- 5) Al_2O_3 doped with 20 mole % Cr,
- 6) Mg rich MgAl_2O_4 ,
- 7) MgZrO_3 ,
- 8) CaZrO_3 ,
- 9) Y_2O_3 . Al_2O_3 ,
- 10) MgTa_2O_6 ,
- 11) CoAl_2O_4 , and
- 12) $\gamma\text{-LiAlO}_2$ (for reference).

Cerium oxide (CeO_2) was added later as a possible alternative for ThO_2 . Candidate No's. 1, 3, 5, and 6 were fabricated at MERDI and the

remainder purchased from commercial sources. The list of candidate materials was formulated based both on results of crucible corrosion tests in FY 78 (many materials were found unsatisfactory and are listed in the Final FY 78 Report) and the MERDI topical report "Evaluation of MHD Materials for Use in High-Temperature Fuel Cells," by Ronald Guidotti dated 15 June 1978.

All candidate materials were characterized prior to corrosion testing utilizing a) Chemical Analysis, b) X-ray Diffraction for Phase Identification, c) Scanning Electron Microscopy (SEM), and d) Surface Area Analysis (B.E.T.). Extremely careful and detailed testing was performed in every case to provide an accurate baseline with which to compare the ceramics after corrosion testing. If detailed chemical analysis was not available on starting materials, emission spectrochemical analysis was performed. Only a portion of the chemical analysis information on hand is reported in Table I. The X-ray diffraction work was performed using unfiltered Cu radiation in order to increase the intensity of any minority phases present. This leads to the presence of K_{β} peaks in the patterns, and for many of the ceramic compositions, complicated (many peaks) patterns result. To enhance analysis and use quantitative match parameters, a computer program was used called the "Johnson Search Match Program," written for JCPDS* and obtained through University Computing Company, Dallas, Texas.

Since the surface area for ThO_2 in Table I is not available, SEM results alone were relied on to define the ThO_2 morphology. The B.E.T.

* JCPDS - International Centre for Diffraction Data. Formerly Joint Committee on Powder Diffraction Standards, 1601 Park Lane, Swarthmore, PA. 19081.

TABLE I.--Properties of Candidate Materials Prior to Testing

Material	Avg. Particle Size	Surface Area	Mesh	Purity (%)	PDF #	Source
Al rich MgAl ₂ O ₄	100 μ mean agglomerate 0.7 μ mean particle	4.59 m ² /g	-100	99.7	21-1152 -Spinel negligible α -Al ₂ O ₃	MERDI-made from reagent grade materials via isopropoxide technique. 45 MgO-55Al ₂ O ₃
ThO ₂	100 μ mean agglomerate 0.4 μ mean particle	NA	-100	Nat. Occurring 99.9%	4-566	RIC/ROC PH10
ZrO ₂ stabilized with Y ₂ O ₃ and Cr ₂ O ₃	4 μ mean particle (0.01- 10 μ range)	10.00 m ² /g	-325	99.9% (Zr .625 Hf .062 Cr .176 Y .177 O ₂)	27-997	MERDI made from: Magnesium Electron Co S grade ZrO ₂ Moly Corp 99.99% Y ₂ O ₃ , and J. T. Baker C.P. grade Cr ₂ O ₃
ZrO ₂ stabilized with CaO	2.3 μ mean particle (0.1-6 μ range) (50% finer than 4 microns)	1.15m ² g	-325	91.5 % ZrO ₂ 2.0 % HfO ₂ 5.0 % CaO ₂ .6 % SiO ₂ .4 % MgO ₂ .2 % Al ₂ O ₃ .15% Fe ₂ O ₃ .15% TiO ₂	24-1074 cubic	Zirconium Corp. of America Zircoa-B

NA = Not Available

TABLE I.--Properties of Candidate Materials Prior to Testing (Continued)

Material	Avg. Particle Size	Surface Area	Mesh	Purity (%)	PDF #	Source
$\text{Al}_2\text{O}_3 + 20 \text{ mol } \% \text{Cr}_2\text{O}_3$	0.4 μ mean particle	2.37 m^2/g	-150	($\text{Al}_{1.8}\text{Cr}_{0.2}$) $_2\text{O}_3$ 99.9% 0.023 % MgO	Dist. 10-173 Distorted $\alpha\text{-Al}_2\text{O}_3$	MERDI made from Reynolds RC-HP-DBM Al_2O_3 J. T. Baker Analyzed Reagent $\text{Cr}(\text{NO}_3)_3$
Mg rich MgAl_2O_4	300 μ mean agglomerate (10-500 μ range) 0.4 μ mean particle (0.1 - 1 μ range)	8.44 m^2/g	-60	99.3%	MgO - 4-829 + Spinel - 21-1152	Dead Sea Periclase Gem 995 MgO Reynolds RC-HP-DBM Al_2O_3 65 MgO - 35 Al_2O_3 MERDI made
-5- MgZrO_3	8 μ mean agglomerate (3-50 μ range) 4 μ mean particle (0.6- 6 μ range)	6.5 m^2/g	-325	98.0% SiO_2 0.8% LOI 1.0%	27-997 (cubic)	Zirconium Corp of America 05-0295-401
CaZrO_3	2.3 μ mean particle (0.1- 6 μ range)	4.0 m^2/g	-325	98.0% SiO_2 0.8% LOI 1.0%	9-364 orthorhombic	Zirconium Corp of America 05-0268-215
$\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	5 μ mean particle	4.3 m^2/g	-150	99.9%	distorted 25-1200	Atomergic Chemetals
MgTa_2O_6	30 μ mean spherical agglomerates 90 μ mean length ta- bular agglomerates 15 μ mean width tabular agglomerates 4 μ mean thickness ta- bular agglomerates	1.1 m^2/g	-150	99.9%	14-680 tetragonal Trace MgO 4-829	Cerac Inc. M-1025 Lot 8095-A-Z
NA = Not Available	0.07 μ mean particle size (0.01 - 2 μ range)					

TABLE I.--Properties of Candidate Materials Prior to Testing (Continued)

<u>Material</u>	<u>Avg. Particle Size</u>	<u>Surface Area</u>	<u>Mesh</u>	<u>Purity (5)</u>	<u>PDF #</u>	<u>Source</u>
Cobalt Aluminate (CoAl ₂ O ₄)	40 μ mean agglomerate (20-100 μ range) 10 μ mean particle (2-30 μ range)	10.8 m ² /g	-100	98.0 %	NA	ROC/RIC Sun Valley, Calif. CO-58
γ -LiAlO ₂	<u>Unground</u> 200 μ mean agglomerate (100-300 μ range) 15 μ mean particle (5-50 μ range) <u>Ground</u> 0.10 μ mean particle 5.51 m ² /g (ROC/RIC)-425 6.61 m ² /g (Ventron)	NA	-400	Li ₂ O 21.4 % purified grade	18-714	Alpha Ventron - #11119 ROC/RIC Li-58

NA = Not Available.

testing is performed out of house, and the instrument is not contained in a hood for proper handling of the powdered alpha-emitting ThO_2 .

Extensive work was performed in characterizing the powders using SEM micrographs. Results were quantified by counting up to 500 particles using random linear intercept techniques. Normally, both an agglomerate size and range were determined, and the morphology was also noted. The agglomerate is a collection of individually discernible particles that are "stuck" together either by sintering or other bonding. The bonding ranges from very strong to fairly light. An examination of SEM micrographs showed the great variety in agglomerates and morphology encountered in this study. (A complete collection of powder micrographs prior to testing can be found in the Annual Status Report, 1 October 1979.) This information can be used in conjunction with the macroscopic surface area and mesh information to form a more complete characterization of powders--both prior and post testing. A partial summary of properties prior to corrosion testing is given in Table I.

The fuel gas atmosphere composition used as a cover gas in the corrosion experiments was selected and submitted to Mr. R. Dudley, U. S. Department of Energy, Division of Fossil Fuel Utilization, 30 March 1979. The composition is based on reformed Naptha at an operating temperature of 700°C and is comprised of the following:

50.2% H_2

10.8% CO

9.5% CO_2

29.5% H_2O

The use of a fuel gas atmosphere necessitated the modification and addition of flow meters, bubblers, heaters and circulators, etc. to the gas supply and disposal trains. Necessary components were ordered, delivered, the system built, and are currently installed on three corrosion test furnaces.

Alumina crucibles were evaporatively and then electrolytically coated with gold (99.99% pure) to a thickness of approximately 0.002 in. with good results. These crucibles were then used as an inert container for the mixed carbonates and the candidate ceramic powder during the high temperature (700°C) testing. The powders were weighed and placed in the covered crucibles with a set volume (also weighed) of a powdered mixture of 62% Li_2CO_3 - 38% K_2CO_3 and heated to 700°C under the fuel gas atmosphere. The powders were initially tested for 200 hours at temperature and evaluated for corrosion, and materials that showed little corrosion were again tested in 1000-hour tests. Post-corrosion examinations were conducted to evaluate corrosion and physical stability. These tests included the following:

- 1) X-ray diffraction to determine phase stability (with computer search/match capability),
- 2) Atomic Absorption (AA) analysis of leached carbonate to determine solubility of ceramic in molten carbonate, and
- 3) SEM determination of morphology and particle size change.

The experimental procedure included the following steps:

- 1) Weigh ceramic crucible and lid to five places;
- 2) Leach with solution of 70 vol.% glacial acetic acid and 30 vol.% acetic anhydride, (Baker Analyzed Reagent Grade) approx. 12 mls/gm CO_3 ;
- 3) Filter using fine porosity filter paper, wash with acetic acid and anhydride solution, and save residue powder and solution;

- 4) Conduct Inductively Coupled Plasma (ICP) analysis or AA chemical analysis on solution for cation concentrations. Combust the filter paper and weigh residue; and
- 5) Conduct tests on powders using X-ray diffraction and SEM analysis.

It was found that there were not quantitative yields on the powders. Sometimes, there was excess carbonate in the powder, losses, etc. such that weight gain or loss was not a viable indication of corrosion effects. The other tests, when evaluated together for a single material, did give very clear indications of chemical and physical stabilities.

Results of the SEM study of particle size changes after 200-hour tests are summarized in Table II. Compositions that show essentially no changes in basic particle size are ZrO_2 stabilized with Y_2O_3 and Cr_2O_3 , ZrO_2 stabilized with CaO , and $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$. Materials with small changes include Al rich MgAl_2O_4 , $\text{Al}_2\text{O}_3 + 20$ mol. percent Cr_2O_3 , and $\gamma\text{-LiAlO}_2$. The $\gamma\text{-LiAlO}_2$ result was unexpected. Materials that exhibited large changes are Mg rich MgAl_2O_4 , CaZrO_3 , MgTa_2O_6 , and CoAl_2O_4 .

Results of the 200-hour X-ray diffraction work are shown in Table III. Materials based on ZrO_2 and Y_2O_3 fared very well-- ZrO_2 stabilized with $\text{Y}_2\text{O}_3 + \text{Cr}_2\text{O}_3$, ZrO_2 stabilized with CaO , and $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$. The compounding of Al_2O_3 with Y_2O_3 seemed to prevent the formation of LiAlO_2 from the Al_2O_3 (at least for the 200-hour tests). The $\gamma\text{-LiAlO}_2$ remained stable, and the formation of Li_2ZrO_3 from the zirconate may indicate that Li_2ZrO_3 may be a good starting material. Looking at the results, it appeared that materials based on Hf, La, Th, Y, Zr, and Ce family of oxides are or would

TABLE II
Particle Size

<u>Material</u>	<u>Prior Test</u>	<u>Post Test (200-hr)</u>	<u>Evaluation</u>
Al-rich $MgAl_2O_4$	100 μm mean agglomerate 0.7 μm mean particle	20 μm mean agglomerate 1.0 μm mean particle	Possible Change
ThO_2	100 μm mean agglomerate 0.4 μm mean particle	4 μm mean particle (0.1 to 10 μm range)	Fair
ZrO_2 stabilized with Y_2O_3 and Cr_2O_3	4 μm mean particle (0.01-10 μm range)	No change	Good
ZrO_2 stabilized with CaO	2.3 μm mean particle (0.1 - 6 μm range)	50 μm mean agglomerate 3.0 μm mean particle	Good
Al_2O_3 + 20 mol % Cr_2O_3	0.4 μm mean particle	10 μm mean agglomerate 0.5 μm mean particle	Possible Change
Mg rich $MgAl_2O_4$	300 μm mean agglomerate 0.4 μm mean particle	No agglomerates 30 μm mean particle (appears layered)	Poor
$MgZrO_3$	8 μm mean agglomerate 4 μm mean particle	50 μm mean agglomerate 4 μm mean particle (narrow distribution)	Small Change
$CaZrO_3$	2.3 μm mean particle	elongated crystallites 20 μm mean lengths, 5 μm mean width plus smaller spherical particles - 2.0 μm mean diameter	Poor
Y_2O_3 . Al_2O_3	5.0 μm mean particle	5.0 μm mean particle	Good

TABLE II (Continued)

<u>Material</u>	<u>Prior Test</u>	<u>Post Test (200-hr.)</u>	<u>Evaluation</u>
MgTa ₂ O ₆	30 μ m agglomerates	No elongated crystals	Poor
	90 μ m mean length tabular agglomerates	0.2 μ m spherical particles	
	15 μ m mean width tabular agglomerates		
	4 μ m mean thickness tabular agglomerates		
	0.07 μ m mean particle size		
CoAl ₂ O ₄	40 μ m mean agglomerate	50 μ m mean agglomerate	Poor
	10 μ m mean particle	6 μ m mean particle (large changes in morphology)	
γ -LiAlO ₂	0.10 μ m mean particle	3 μ m agglomerate	Change
		0.2 - 0.5 μ m particle (depends on LiAlO ₂ source evaluations difficult)	

TABLE III
X-ray Phase Identification (Powders)

<u>Material</u>	<u>Prior Test</u>	<u>Post Test (200-Hr.)</u>	<u>Evaluation</u>
Al rich MgAl_2O_4	21-1152 Spinel	19-713 $\alpha\text{-LiAlO}_2$ 21-1152 minor	Poor
ThO_2	4-556	Unchanged	Good
ZrO_2 stabilized with $\text{Y}_2\text{O}_3 + \text{Cr}_2\text{O}_3$	27-997 (cubic)	27-997	Good
ZrO_2 stabilized with CaO	24-1074 (cubic)	24-1074	Good
$\text{Al}_2\text{O}_3 + 20 \text{ mol } \%$ Cr_2O_3	Distorted 10-173 ($\alpha\text{-Al}_2\text{O}_3$)	19-713 $\alpha\text{-LiAlO}_2$	Poor
Mg rich MgAl_2O_4	4-829 MgO +21-1152 Spinel	major 19-713 $\alpha\text{-LiAlO}_2$ minor 4-829 MgO	Poor
MgZrO_3	27-997 cubic MgZrO_3	9-364 orthorhombic zirconate	Fair
CaZrO_3	9-364 orthorhombic CaZrO_3	20- Li_2ZrO_3 10-461 $\text{K}_2\text{ZrSi}_3\text{O}_9$ 20-647 ZrO_2	Poor Li_2ZrO_3 may be stable
$\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	25-1200 distorted Y_2O_3	25-1200	Good
MgTa_2O_6	14-680 tetragonal minor 4-829 MgO	33-1198 KTaO_3 2-822 KLiTaO	Poor
CoAl_2O_4	10-458 cubic	19-713 $\alpha\text{-LiAlO}_2$ major 10-450 CoAl_2O_4	Poor
$\gamma\text{-LiAlO}_2$	18-714 major $\gamma\text{-LiAlO}_2$ 19-713 small $\alpha\text{-LiAlO}_2$	unchanged	Good

be corrosion resistant as would some oxides in combination with Li, e.g., LiAlO_2 and perhaps Li_2ZrO_3 .

Results of the AA analysis of filtered carbonate leaches are shown in Table IV. The results of tests for different elements are normalized with respect to the amount of sample and carbonate used and also the surface area of the sample. Good correlation with Table II and Table III can be made. $\text{ZrO}_2 + \text{CaO}$ tested well in the other tests but showed that Ca is being taken into the carbonate, perhaps the Ca is being replaced with Li. Based on the ZrO_2 stabilized with Y_2O_3 and Cr_2O_3 , it seems that ZrO_2 stabilized with Y_2O_3 would be preferable over ZrO_2 stabilized with Ca. It is interesting to note that the $\gamma\text{-LiAlO}_2$ sample showed Al but didn't seem to change phases (see Table III) although the particle size changed slightly.

A compilation of positive and negative results after the post 200-hour evaluations is given in Table V. Materials that ranked good or needed additional information were tested in 1000-hour corrosion tests. Materials selected were ZrO_2 stabilized with $\text{Y}_2\text{O}_3 + \text{Cr}_2\text{O}_3$, Y_2O_3 , Al_2O_3 , $\gamma\text{-LiAlO}_2$, ThO_2 , $\text{ZrO}_2 + \text{CaO}$, and CeO_2 . Cerium oxide (CeO_2) was added to check if it would be a suitable replacement for ThO_2 . Uranium oxide (depleted UO_2) might also be a suitable replacement for the ThO_2 .

Results of 1000-hour SEM, X-ray and chemical analysis of the leached carbonates are given in Tables VI, VII, and VIII.

The $\text{ZrO}_2 + \text{Ca}$ had a reasonably small increase in mean particle size (from $2.3 \pm 4.0 \mu\text{m}$) but appears to be slowly changing its phase while losing calcium to the carbonate. The $\gamma\text{-LiAlO}_2$ particles

TABLE IV

Chemical Analysis of Filtered Carbonate
After 200-Hour Tests

<u>Material</u>	<u>Original Sample Wgt.(gm)</u>	<u>Original Sample Surface area (m²)</u>	<u>Weight Carbonate (gm)</u>	<u>gm cation dissolved gm sample</u>		<u>gm cation dissolved gm carbonate-m²</u>
Al rich MgAl ₂ O ₄	6.78983	31.17	25.20304	1.0 x 10 ⁻²	Al	8.7 x 10 ⁻⁵
				1.3 x 10 ⁻²	Mg	1.1 x 10 ⁻⁴
ZrO ₂ +Y+Cr	10.16853	101.69	23.68196	2.9 x 10 ⁻⁵	Zr	1.2 x 10 ⁻⁷
				3.3 x 10 ⁻⁵	Cr	1.4 x 10 ⁻⁷
ZrO ₂ +Ca	15.53333	17.86	21.113006	2.2 x 10 ⁻⁵	Al	9.0 x 10 ⁻⁷
				2.2 x 10 ⁻⁴	Mg	9.0 x 10 ⁻⁶
				2.6 x 10 ⁻⁵	Zr	1.1 x 10 ⁻⁶
				2.7 x 10 ⁻³	Ca	1.1 x 10 ⁻⁴
Al ₂ O ₃ +Cr ₂ O ₃	6.58426	15.60	24.44155	6.2 x 10 ⁻³	Al	1.1 x 10 ⁻⁴
				9.5 x 10 ⁻⁵	Mg	1.6 x 10 ⁻⁶
				3.8 x 10 ⁻⁵	Cr	6.5 x 10 ⁻⁷
Mg rich MgAl ₂ O ₄	8.15150	68.80	24.99691	1.2 x 10 ⁻²	Al	6.4 x 10 ⁻⁵
				1.6 x 10 ⁻²	Mg	8.6 x 10 ⁻⁵

TABLE IV (Cont.)

Material	Original Sample Wgt. (gm)	Original Sample Surface area (m ²)	Weight Carbonate (gm)	<u>gm cation dissolved</u> <u>gm sample</u>		<u>gm cation dissolved</u> <u>gm carbonate-m²</u>
MgZrO ₃	8.87663	57.70	14.41237	2.0 x 10 ⁻⁵	Mg	2.2 x 10 ⁻⁷
				< 2.1 x 10 ⁻⁵	Zr	< 2.2 x 10 ⁻⁷
CaZrO ₃	9.36158	37.45	19.83440	9.1 x 10 ⁻⁴	Zr	2.2 x 10 ⁻⁵
				2.0 x 10 ⁻⁴	Ca	2.6 x 10 ⁻⁶
Y ₂ O ₃ .Al ₂ O ₃	8.12150	34.92	23.92531	6.5 x 10 ⁻⁵	Al	6.3 x 10 ⁻⁷
MgTa ₂ O ₆	14.31856	15.55	17.90647	3.9 x 10 ⁻³	Mg	2.0 x 10 ⁻⁴
CoAl ₂ O ₄	6.99136	75.51	25.3476	3.3 x 10 ⁻³	Al	1.2 x 10 ⁻⁵
γ-LiAlO ₂ ** (ROC/RIC)	1.35335	7.46	12.57170	3.8 x 10 ⁻²	Al	5.4 x 10 ⁻⁴
γ-LiAlO ₂ ** (Ventron)	8.20819	54.73	29.67537	9.2 x 10 ⁻³	Al	6.8 x 10 ⁻⁵
ThO ₂ *	13.72829	N.A.	17.90325	2.9 x 10 ⁻⁵	Th	NA

NA = Not Available

* = ICP Technique

** = Levels may be high due to loss of fine particles through filters.

TABLE V
Compilation of Evaluations (after 200 hours)

<u>Good</u>	<u>Questionable or Inadequate Information</u>	<u>Poor</u>
ZrO ₂ + Y ₂ O ₃ and Cr ₂ O ₃	ThO ₂	Al rich MgAl ₂ O ₄
Y ₂ O ₃ + Al ₂ O ₃	ZrO ₂ + CaO	Al ₂ O ₃ + Cr ₂ O ₃
	MgZrO ₃	Mg rich MgAl ₂ O ₄
		CaZrO ₃
γ-LiAlO ₂ (past performance)	γ-LiAlO ₂	MgTa ₂ O ₆
		CoAl ₂ O ₄

TABLE VI
Particle Size

<u>Material</u>	<u>Prior Test</u>	<u>200 hrs</u>	<u>1000 hrs</u>
ZrO ₂ + Ca	2.3 μm mean particle (0.1 - 6 μm range)	50 μm agglomerate 3.0 μm mean particle	4.0 μm mean particle (0.1 - 10 μm range)
γ-LiAlO ₂	0.10 μm mean particle	3 μm agglomerate 0.2 - 0.5 μm particle (depends on LiAlO ₂ source)	0.4 μm mean particle (was 0.2 in 200-hr test) 0.2 - 10 μm range - some bipyramids
Y ₂ O ₃ . Al ₂ O ₃	5.0 μm mean particle	5.0 μm mean particle	40 μm mean particle (0.1 - 100 μm range) large crystals of polyhedrons and blocklike plates.
ThO ₂	100 μm mean agglom- erate 0.4 μm mean particle	4 μm mean particle (0.1 - 10 μm range) platelike morphology	4 μm mean particle (0.1 - 10 μm range) platelike
CeO ₂	2 μm mean particle (0.1 - 10 μm range) varied morphology	NA	5 μm mean particle (0.1 - 20 μm range) all cubic bipyramids
ZrO ₂ + Y + Cr	4 μm mean particle (0.01 - 10 μm range)	4 μm mean particle (0.01 - 10 μm range)	5 μm mean particle (0.1 - 10 μm range) some fuzzy, some bipyramids

NA = Not Available

TABLE VII

X-ray Phase Identification (powders)

<u>Material</u>	<u>Prior Test</u>	<u>Post 1000-hr test</u>
ZrO ₂ + Ca	24-1074 (cubic)	24-1074 with extra unidentified peaks
γ-LiAlO ₂	18-714 major γ-LiAlO ₂ 19-713 small α-LiAlO ₂	18-714 γ-LiAlO ₂
Y ₂ O ₃ + Al ₂ O ₃	25-1200 distorted Y ₂ O ₃	25-1200 with doublet 100% peaks
ThO ₂	4-556	4-556 (Unchanged)
CeO ₂	4-593 (cubic)	4-593 (cubic) (Unchanged)
ZrO ₂ + Y + Cr	27-997 (cubic)	27-997 (cubic) (Unchanged)

TABLE VIII

Chemical Analysis of Filtered Carbonate
After 1000 Hour Tests

<u>Material</u>	<u>Original Sample Wgt. gm</u>	<u>Original Sample Surface Area (m²)</u>	<u>Weight Carbonate (gm)</u>	<u>gm cation dissolved gm sample</u>		<u>gm cation dissolved gm carbonate-m²</u>
ZrO ₂ +Y+Cr	12.35110	123.51	23.65795	5.1 x 10 ⁻⁵	Zr*	2.2 x 10 ⁻⁷
				5.7 x 10 ⁻⁶	Cr ⁺	2.3 x 10 ⁻⁸
				NA	Y	NA
ZrO ₂ +Ca	12.80273	14.72	24.52145	2.3 x 10 ⁻⁶	Zr*	8.2 x 10 ⁻⁸
				1.3 x 10 ⁻²	Ca ⁺	4.9 x 10 ⁻⁴
Y ₂ O ₃ .Al ₂ O ₃	7.17449	30.85	25.64020	1.5 x 10 ⁻⁴	Al ⁺	1.4 x 10 ⁻⁶
				NA	Y	NA
CeO ₂	4.98102	NA	26.61590	6.2 x 10 ⁻³	Ce*	NA
γ-LiAlO ₂ ** (Ventron)	3.32436	21.97	22.46116	5.0 x 10 ⁻³	Al ⁺	2.0 x 10 ⁻⁵
ThO ₂	11.01022	NA	19.54386	5.7 x 10 ⁻⁵	Th	NA

NA = Not Available

* = ICP

** = Results maybe high due to loss of small particles through filters

+ = Atomic Absorption

increased from a 0.10 μm to 0.40 μm mean particle size after 1000 hours including the formation of some large (up to 10 μm) bipyramids (see Figures 1 to 3). There was a possible loss of the small amount of $\alpha\text{-LiAlO}_2$ present in the sample before testing. The particle growth was accompanied by a significant amount of Al in the melt. The Y_2O_3 . Al_2O_3 looked very good at 200 hours; and the chemical leaching was good to 1000 hours; but between 200 and 1000 hours, there was rapid particle growth (5.0 - 40 μm) with some changes occurring in the X-ray pattern. The ThO_2 exhibited initial particle growth from 0 to 200 hours but appeared stable between 200 and 1000 hours with a mean particle size of 4.0 μm with little solubility and no phase change. Similarly, the CeO_2 had no phase change but showed substantial solubility and particle growth (2.0 - 5.0 μm). The $\text{ZrO}_2 + \text{Y} + \text{Cr}$ had low solubility, little particle growth (4.0 - 5.0 μm) and unchanged X-ray pattern. It must be pointed out that the $\text{ZrO}_2 + \text{Y} + \text{Cr}$ had a much larger mean particle size than the $\gamma\text{-LiAlO}_2$ (4.0 versus 0.1 μm), but the $\text{ZrO}_2 + \text{Y} + \text{Cr}$ had a larger surface area (10 m^2/g versus 5.51 - 6.61 m^2/g) than the $\gamma\text{-LiAlO}_2$.

A more graphic representation of the particle size and chemical analysis of the melt is presented in Figures 8 through 12. Figures 8 and 9 show the relative particle sizes prior to testing and after 200 and 1000 hour tests. Figure 10 and 11 show the measured concentrations of various cations in the leached carbonates after 200 hours. Figure 12 shows the chemical analysis of the leached carbonate after the 1000-hour test.

200x

2000x

Figure 1a.--Prior Testing γ -LiAlO₂.

200x

1000x

Figure 1b.--Post 1000-hr corrosion test γ -LiAlO₂.

200x

1000x

Figure 2a.--Post 1000-hr corrosion test γ -LiAlO₂
(Note bipyramidal grains)

5000x

Figure 2b.--Post 1000-hr corrosion test γ -LiAlO₂

10,000x

Figure 3.--Post 1000-hr. corrosion test γ -LiAlO₂.

50x

500x

Figure 4a.-- γ -LiAlO₂ fibers fired to 1350°C.

50x

Figure 4b.-- γ -LiAlO₂ fibers fired to 1350°C - (note the "balls" of rolled fibers).

100x

Figure 5.-- γ -LiAlO₂ fibers fired to 1350°C
70° tilt Dynamic Focus

200x

Figure 6a.-- γ -LiAlO₂ fibers fired to 1350°C - fiber "mat".

1000x

Figure 6b.--"Close-up" of γ -LiAlO₂ fiber "mat".

1000x

Figure 7a.--Spinel fibers after 200-hr corrosion test
(Note presence of carbonates.)

1000x

Figure 7b.--Spinel fibers after 200-hr corrosion test.

POST 200-HR. CORROSION TEST

Figure 10.--Chemical analysis of cation concentrations found in leached carbonates.

gm CATION DISSOLVED
gm SAMPLE

POST 200-HR. CORROSION TEST

Figure 11.--Chemical analysis of cation concentrations found in leached carbonates.

gm CATION DISSOLVED
gm SAMPLE

gm CATION DISSOLVED
gm SAMPLE

POST 1000-HR. TESTS

Figure 12.--Chemical analysis of cation concentrations found in leached carbonates.

These results are harmonious with results of corrosion tests recently reported by United Technologies Corporation* (UTC) where LiAlO_2 and an "alternate" ceramic material were immersed in electrolyte at 760°C under both anode and cathode gases for times up to 1000 hours. Characterization of their post-test results showed that changes in particle morphology, surface area and particle size distribution had occurred. UTC tentatively concluded the process to be solubility rate controlled.

It is inherent in all systems where there are dispersed particles of varying size having some solubility in a surrounding medium that the smaller particles dissolve and precipitate onto larger particles. This process is continuous and is driven by a reduction in interfacial energy. As the particle sizes increase, the driving force is less and the rate slows such that the final state of a single large particle may never practically occur.

Initially there should be a particle size decrease of both large and small particles as solid material is dissolved in the liquid; this will occur until the solution is saturated. This process could actually result in a smaller mean particle size and will skew the size distribution. After saturation occurs the precipitation process can begin with resulting particle growth.

* Development of Molten Carbonate Fuel Cell Power Plant Technology, Quarterly Technical Progress Report No. 1 - October-December, Contract DE-AC-01-79ET 15440, March 1980 - UTC, P.O. Box 109, South Windsor, Conn. 06074, pg. 2-3.

UTC reports the approximate mean particle radius can be found by one of the following relationships:

$$\bar{r}_{(t)}^3 = \bar{r}_0^3 + \frac{8DC\sigma\Omega}{9RT} t \quad (\text{Diffusion Controlled})$$

$$\bar{r}_{(t)}^2 = \bar{r}_0^2 + \frac{8KC\sigma\Omega}{9RT} t \quad (\text{Solubility Controlled})$$

where

- r = mean particle size
- r_0 = starting mean particle size
- D = diffusion constant
- C = solubility
- σ = surface energy
- K = rate constant for solubility
- Ω = molar volume
- R = gas constant
- T = temperature, °K
- t = time

Note: D , C , K are functions of Temperature (T).

In general, the particle size distribution is important and has been considered by Greenwood* in the diffusion limited case for spherical particles. For anisotropic crystallographic faces the dissolution and reprecipitation would be different for the different faces of the crystals.

* G. W. Greenwood, "The Growth of Dispersed Precipitation in Solution," Acta metallurgica Vol. 4, May 1958, page 243.

This effect has been seen in the bipyramid shaped particles resulting in our 1000-hour tests, and the theory is inexact for this case. However, a careful measurement of the particle size as a function of time should indicate whether the diffusion or solubility controlled equation fits the data. UTC calculated a diffusion rate of $\sim 10^{-10}$ cm²/sec. which seemed to be low for a liquid and they therefore conclude solubility control.

There may be ways to slow (but not stop) the dissolution process. The starting particle size could be increased to minimize the percentage increase over a time period. The temperature could be changed, the melt doped with impurities to change the solubilities, or the surface energy modified via structural changes. It is felt that these are second order effects and possibly the best way would be to reduce the solubility by modifying the melt composition; perhaps a Na₂CO₃ and K₂CO₃ mixture would have less solubility (the melting temperature could be lowered with the adding of CaCO₃) of the metal oxides. The Li₂CO₃ - Na₂CO₃ mixture probably is a "better" electrolyte, but our x-ray phase change study indicates that the lithium is involved in a majority of deleterious reactions and is the most reactive of the electrolyte species.

We would recommend that corrosion studies should be performed on our "best" materials using other electrolyte compositions.

Although criteria have not been set for ranking the overall corrosion resistance of materials in molten carbonate, a judgment as to ranking is tabulated in Table IX. Use of materials ranking 5, 6, and 7 would be questionable if used as fine powders in liquid 62 Li_2CO_3 - 38 K_2CO_3 at 700°C under a fuel gas atmosphere. In less severe applications they might be acceptable. Compositions ranked 1 through 4 could be useful as fine powders and even more corrosion resistant in more monolithic forms. Some of the remaining compositions (Al rich MgAl_2O_4 , Al_2O_3 + Cr_2O_3 , Mg rich MgAl_2O_4 , CaZrO_3) including Al_2O_3 are ranked as poor under the test conditions but could and do find service in their dense monolithic state.

Corrosion tests were also conducted for 1000-hour duration on polycrystalline ceramic fibers made from $\gamma\text{-LiAlO}_2$, CeO_2 , and ZrO_2 + Y + Cr. These tests were to see if the physical integrity of fibers could be maintained if they were made from corrosion resistant materials. The compositions chosen were two compositions that ranked good ($\gamma\text{-LiAlO}_2$ and ZrO_2 + Y + Cr) and one that ranked questionable (CeO_2) in the 1000-hour powder corrosion tests. The CeO_2 fibers were sintered at 1760°C, the ZrO_2 + Y + Cr fibers were sintered at 1650°C, and one sample of LiAlO_2 fibers was sintered at 1550°C while the other sample of LiAlO_2 fibers was sintered at 1500°C. From SEM examinations of the microstructures, we conclude that lower temperature firings probably would have been desirable because the samples retain a more fibrous nature when only sintered enough to "stick" individual particles together and not begin densification and coalescence of the smaller fibers.

The microstructure of the CeO_2 sample prior to testing (fuel gas atmosphere, 700°C) is shown in Figure 13a. The microstructure after testing for 1000 hours is shown in Figures 13b to 13d. Figures 13c

TABLE IX
Compilation of evaluations After 1000-Hours

Good

1. $\text{ZrO}_2 + \text{Y} + \text{Cr}$

2 or 3. ThO_2

2 or 3. $\gamma\text{-LiAlO}_2$

4. $\text{ZrO}_2 + \text{Ca}$

Questionable-Use

5. CeO_2

6 or 7. $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$

6 or 7. MgZrO_3

Poor

MgTa_2O_6

CoAl_2O_4

CaZrO_3

100x

500x

Figure 13a.-- CeO_2 fibers before testing

100x

500x

Figure 13b.-- CeO_2 fibers before testing

100x

500x

Figure 13c.--CeO₂ fibers after 1000-hr test

1500x

Figure 13d.--CeO₂ fibers after 1000-hr test

and 13d indicate grain growth (approximately 12.7 μm to 20.0 μm median), grooving of the grain boundaries and swelling of the small grains that are embedded in the larger grains. These smaller grains may be a second phase material in the CeO_2 . The large fiber chains do not completely disintegrate into the small grains of which they are aggregated.

The microstructure of the $\gamma\text{-LiAlO}_2$ prior to testing is shown in Figures 14a and 14b for 1550°C sintered fibers and 14d for 1500°C sintered fibers. The microstructure after corrosion testing is shown in Figure 14c for the 1550°C material and Figure 14e for the 1500°C material. For both type of materials the median grain size increased. Fibers with more than 5 to 10 grains through their diameter held together well; fibers with less grains through their diameters appeared to fragment into shorter lengths of approximately 10 to 15 grains long. The bonding between the individual grains seemed to decrease somewhat. The median grain size increased from 0.80 μm to 2.8 μm for the 1550°C fired fibers and from 0.82 μm to 1.7 μm for the 1500°C fired fibers. The median figure does not reflect the range of particle size which increased due to an appreciable amount of large (6 to 10 μm) particles.

The microstructure of the $\text{ZrO}_2 + \text{Y} + \text{Cr}$ sample prior to testing is shown in Figures 15a and 15b. The microstructure after corrosion testing is shown in Figures 15c and 15d. It appears that the smaller diameter fibers are fragmented and through the leaching and washing process are no longer present in the larger clumps of materials. The larger diameter (many particle) fibers were much in evidence and to lower magnification optical observation the sample still appeared to be quite fibrous in nature. The median grain size increased from 1.8 μm to 3.5 μm after testing. The morphology of the individual grains changed

3000x

Figure 14a.-- γ -LiAlO₂ fibers before testing (sintered at 1550°C)

3300x

Figure 14b.-- γ -LiAlO₂ fibers before testing (sintered at 1550°C).

3000x

Figure 14c.-- γ -LiAlO₂ fibers after 1000-hr. test

100x

500x

Figure 14d.-- γ -LiAlO₂ fibers before testing (sintered at 1500°C)

Figure 14e.-- γ -LiAlO₂ fibers after 1000-hr test

Figure 14f.-- γ -LiAlO₂ after 1000-hr test

500x

Figure 15a.--ZrO₂ + Y + Cr fibers before testing

1000x

Figure 15b.--ZrO₂ + Y + Cr fibers before testing

100x

500x

Figure 15c.-- $\text{ZrO}_2 + \text{Y} + \text{Cr}$ fibers after 1000-hr test

1000x

Figure 15d.-- $\text{ZrO}_2 + \text{Y} + \text{Cr}$ fibers after 1000-hr test

from smooth and rounded to angular with many bi-pyramidal grains. The surviving large fibers had approximately 30 to 60 μm diameters.

For all the polycrystalline fibers tested, it is concluded that particle growth (re-crystallization) occurs to varying degrees, and bonding strength probably decreases. Small diameter fibers are fractionated; this may be due to handling (leaching, filtering, etc.), chemical attack, or thermal expansion mismatches between the carbonate and the ceramics. Larger diameter fibers appear to hold together much better, but proper documentation of this conclusion would take much more testing.

B. Task 2 - Fiber Formation

Work has continued on the development of polycrystalline ceramic fibers. It was in response to the need for low-cost ceramic fibers for use in the molten carbonate fuel cell that Mr. Ted Morse of MERDI invented a novel method for the formation of ceramic fibers. Mr. Morse assigned his patent right to the United States Department of Energy on 16 August 1978. Constant improvement of the process and apparatus is taking place, but the basic process is as follows.

1. Process

A slurry (similar to household paint) is made of finely ground ceramic powder, acetone, and liquid acrylic binder. The mixture contains ceramic powder, $\sim 1/3$ by weight of the amount of ceramic oxide powder. It has been found that the acetone portion is the easiest to vary in the mixture and has an effect on the final product. The mixture is next placed in a mill where agglomerates are broken up and an uniform slurry obtained. The slurry can then be poured or dripped into a container which is rotating on its own axis at high speeds. This process is illustrated in Figure 16. The slurry is forced against the walls with a radial acceleration from 10^7 (rev./min)² x inches to 10^{15} (rev./min.)² x inches. The container has holes in the exterior walls (< 2 mm but $>$ largest ceramic powder size) through which the slurry is forced. During this process, fibers of acrylic bound ceramic are formed in the air surrounding the spinner as the volatile acetone evaporates. The resulting mat of fibers formed are shown in Figures 4, 5, 6, and 17. Changes in the speed of the spinner, particle size distribution of the ceramic, and slurry viscosity all influence the morphology of the resulting fiber mat. These fibers in their green state

Figure 16.--Fibers are Formed by Spinning Slurry.

Figure 17.--Closeup View of 'Green' Fibers Collected Around Perimeter of Spinning Apparatus.

can be easily handled, aligned, or pressed lightly to form desirable configurations prior to high temperature sintering. The high temperature treatment (much lower temperature than needed to melt the ceramic) burns off the binder and sinters the particles into a polycrystalline fiber.

Fibers have been made from Al_2O_3 , MgO , LiAlO_2 , MgAl_2O_4 , NiO , and CeO_2 . It appears this process is suitable for any ceramic powder mixture that can be made to sinter to itself. Scanning electron micrographs of fired Al_2O_3 fibers are shown in Figure 18a and 18b and micrographs of $\gamma\text{-LiAlO}_2$ are shown in Figures 4, 5, and 6. Fiber diameters can vary from 1 μm to 20 μm and can have length to diameter aspect ratios $> 100 : 1$. Bundles of fibers can be up to a foot in length.

Various binders have been tried including Rohm and Haas B-72 and B-82.*

A batch formation found to work well with Al_2O_3 , LiAlO_2 , and spinel is as follows:

Ceramic Powder	30 w/o
Acetone	60 w/o
Liquid Binder	10 w/o

During the contract period, the quality control of the forming process was found to be extremely variable. Much effort was expended to identify and correct this condition. The primary erratic variables are slip viscosity, acetone grade, and ceramic powder hydration.

*Rohm and Haas Co.
Independence Mall West
Philadelphia, Penn. 19105

1 μm

Figure 18a.--SEM Photomicrograph of Al_2O_3 sintered fiber - 10,300x.

10 μm

Figure 18b.--SEM Photomicrograph of Al_2O_3 sintered fiber mat - 760x.

These variables have been controlled by the following actions:

- 1) purchased a "Brookfield" viscometer (using MERDI internal funds) to monitor slip viscosity,
- 2) used a single grade acetone (J. T. Baker NF grade), and
- 3) add the binder just before fiber spinning and make small batches if hydration appears to be a problem (MgO is very sensitive to hydration).

2. Strength Tests

Tensile strength test bars have been fabricated of fibers made of three materials: 1) α -Al₂O₃, 2) MgO, and 3) γ -LiAlO₂. Bundles of green fibers were laid up as "uniaxially" as possible, lightly pressed, and then sintered at high temperatures. The samples were then shipped to Richard E. Tressler, Associate Professor of Ceramic Engineering, Pennsylvania State University for evaluation. Tensile strength tests, bonding strength tests, acoustic emission analysis during strength testing, and scanning electron microscopy of fracture surfaces were performed at Pennsylvania State. This work is complete, and Dr. Tressler's report is included as Appendix B to this report. (Initial results were reported in Technical Status Report No. 10, 15 February 1980)

MERDI's interpretation of Tressler's results are the following:

- 1) Fiber bundles are complex tows of fibers of variable diameter with discontinuous fibers which are misaligned, and the bundles also contain beads of material. Alignment of the bundles does not, in general, align a significant fraction of individual fibers. There is much lateral bonding and 3-D nature within fiber bundles. The alignment of fiber bundles results in sintered columns and also large pore channels normal to the fracture surface.

The columns when examined under high magnification (e.g. 10,000x) have an innate fine 3-D network of fibers.

2) Measured yield strengths of the fiber compacts are not simple linear functions of density and in fact seem to be functions of some unspecified fabrication parameter. If all the fibers were aligned, it could be assumed that the cross-sectional area is proportional to the sample density. If this assumption is correct, when the breaking stress is calculated from the breaking load, the stress values should be approximately the same and independent of the density. The calculated stress values are not independent of density and in fact vary widely for samples of the same density. Hence, calculated stress values are not applicable to individual fibers.

A literature survey indicates large samples of high density (>98 percent theoretical) alumina have been tested in tensile tests at room temperature with results varying from 22,000 to 50,000 psi.* Ceramics are typically weak in tension, but if loaded in a bending configuration, the strengths of polycrystalline samples increase to the 60,000 psi range. If MERDI's single fibers have a large number of grains across their cross-section, it would be expected that their tensile strengths (Al_2O_3) should be in the 20,000 psi range. However, if they are extremely small and consist of single grains, they might

* Engineering Properties of Selected Ceramic Materials
American Ceramic Society, 1966 pp, 5.4.1-9

be extremely flexible owing to the fact that large deflections are possible at small strain values but would have strengths governed by the strength of the grain boundary (approximating a bi-crystal), and strengths might be quite low in tension. The nature of the loads encountered in a molten carbonate fuel cell tile during actual operation is not known at this time.

3) The measured strengths of the 3-D compacts (not individual fibers) can be as high as 355 psi for MgO , 713 psi for LiAlO_2 , and 9,348 psi for Al_2O_3 .

4) Tressler recommends the elimination of the shipping of fibers prior to strength testing and the testing of extremely small gauge length fibers or bundles (utilizing a small horizontal whisker testing apparatus might give applicable single fiber strength values).

IV. CONCLUSIONS

Powders of $\text{ZrO}_2 + \text{Y}_2\text{O}_3 + \text{Cr}_2\text{O}_3$, ThO_2 , and $\gamma\text{-LiAlO}_2$ show the least corrosion response to 62 Li_2CO_3 -38 K_2CO_3 at 700°C under a fuel gas atmosphere for 1000 hours. These materials should be tested in other electrolyte compositions--e.g., K_2CO_3 - Na_2CO_3 mixture with or without CaCO_3 . Other ceramic compositions studied may have acceptable corrosion resistance if in dense monolithic form. Lithium zirconate (Li_2ZrO_3) appears to be a stable corrosion product, and its use should be investigated further.

The strengths of ceramic fiber mats produced at MERDI are dependent upon unspecified structure and/or fabrication parameters. Selected fiber mats have tested strengths of up to 10,000 psi, but individual fiber strengths could not be determined under the test conditions used. One-thousand hour corrosion tests on fibers of the "best" compositions indicated smaller diameter fibers fragment into shorter lengths while large diameter (>5-10 grains cross-section) hold together well.

APPENDIX A

PROJECT MILESTONE CHART

HIGH TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

TASK 1. MATERIALS IDENTIFICATION
REPORT DUE ○

Figure A-1.--Project Milestone Chart

HIGH TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT	

TASK 1. MATERIALS IDENTIFICATION
REPORT DUE ○

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1979

1980

MONTH

M. A. M. J. J. A. S. O. N. D. J. F.

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☒ **✓**

B.E.T.

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A-2

9-12-78 2-000-112-A

PROJECT MILESTONE CHART

HIGH-TEMPERATURE FUEL CELL RESEARCH AND DEVELOPMENT

TASK 2. FIBER PREPARATION
REPORT DUE ○

YEAR
MONTH

1979

1980

M A M J J A S O N D J F

MAJOR MILESTONES AND
DECISION POINTS

CANDIDATE MUST PASS ALL POST
200 HOUR TESTS

2.1 PREPARE FIBERS

2.2 EVALUATE FIBERS

. TENSILE STRENGTH TEST
(SUBCONTRACT)

. S.E.M.

. 1000 HOUR TESTS

. Post 1000 Hour Exam

. S.E.M.

. X-RAY DIFFRACTION

. A.A.

. 100 GRAM SAMPLES

A-3

Figure A-3.--Project Milestone Chart

APPENDIX B

Final Report to
MERDI
Subcontract No. 9-A641-F
by
R. E. Tressler

"Mechanical Properties of Fibrous Composites"

March 14, 1980

INTRODUCTION

The original objective of this study was to measure the strengths of individual, polycrystalline oxide fibers prepared by MERDI and to relate those strengths to processing variables. However, in our earlier work (October 3, 1979, and January 17, 1980, letter reports), it became obvious that the fiber bundles were complex tows of fibers of variable diameter with discontinuous fibers misaligned, and they also contained beads of material. Thus, we agreed to concentrate on measuring strengths of composite coupons which contained more or less aligned bundles which were compacted and fired. From the load deflection curves and simultaneous acoustic emission counts, we hoped to determine the stress at first fiber fracture and the ultimate strengths of the composites. We agreed to examine the fracture surfaces of these materials with the SEM to try to determine the number of fibers or bundles, and to attempt to extract weakest and average fiber or bundle strengths.

Our results for the alumina materials were reported in the first two letter reports and will not be repeated here except in the discussion and summary of the various materials which we examined. In the following, I will briefly review the characteristics of the materials that we tested, describe our test procedures, present the results of our experiments since the January 17, 1980, letter report, and discuss and compare the results from all of the testing.

MATERIALS

The first reliable data were generated from alumina fiber coupons of three different densities (January 17, 1980, report). The microstructures were quite irregular consisting of a range of fiber diameters

with fibrils and clumps and misalignment of the fibrils and fibers as shown in that report. The densities corresponded to ~42, ~50, and ~67% of the theoretical density for α -alumina. The highest density material was reminiscent of a porous compact in the early stages of sintering with some suggestion of fiber relics.

The second major group of samples were MgO. The 12 samples had densities ranging from 1.12g/cc to 1.52g/cc. The strengths of these samples fell into two groups (see Table 1); thus, our SEM investigations concentrated on one sample from each group (sample number 4 from the high strength group and sample 7 from the low strength group). Figures 4-6 illustrate the microstructures of the MgO samples as viewed from the fracture surfaces (with a gold coating applied).

As one can see from the low magnification micrographs of MgO samples 4 and 7, the microstructure is composed of apparently well-sintered clumps or balls with fibrous material interspersed. We do not see well-aligned fibers or bundles of fibers. Sample 7 appears to have a higher fraction of fibrous material exposed on the fracture surface than does sample 4 (compare Figure 4e with Figures 5d and 5e). It is not clear exactly what features on the fracture surface are caused by the propagating crack. One cannot decide whether or not these sintered clumps were attached to fibers which were broken during the fracture process. However, in Figure 4e (sample 4) in the lower right part of the picture it appears that there are asperities on the surfaces of the clumps which may have been attached to fibers.

As was the case with the alumina samples, although there is a fibrous nature to the material, the fibers are not well-aligned, and it is hopeless to try to determine individual fiber strengths. In the higher

magnification micrographs, one can get the sense of pore channels running perpendicular to the fracture surface, parallel to the specimen length. However, there is much lateral bonding and 3-D nature to the fiber orientation.

The LiAlO_2 samples were also roughly grouped into a high strength group and a low strength group (Table 2). Thus, we examined #2 from the low strength group and #6 from the higher strength group. Figures 7-9 illustrate the microstructures of these two samples. Sample #2 has a quite uniform microstructure composed of fairly distinguishable fibers as evidenced by the cylindrical shapes in Figure 7b and the pore channels perpendicular to the fracture surface. The fibers fractured transgranularly (Figures 7b and 7e) revealing intergranular porosity. The fibers are sintered together forming a rigidized fiber mat. From Figures 7b and 7e one can estimate these fibers to be $\sim 1.9 \times 10^{-3}$ inches in diameter, a very rough estimate.

The low magnification micrographs from sample #6 appear similar to the corresponding ones from sample #2. There are obviously pore channels normal to the fracture surface; but at higher magnifications (Figures 8e, 8f, 9c, and 9d), one can see that the microstructure is much finer. The features that look like fibers at low magnifications are, in fact, composed of fibrils arranged in a 3-D network (Figures 8f and 9d). These clusters of fibrils are sintered into a 3-D composite. Sample #6 appears to be much lower in density than #2 which is confirmed in Table 2. Are these two different firing conditions or sample compositions leading to these differences in the microstructures which apparently result in different σ_F vs. density relationships?

The last lot of samples received were α - Al_2O_3 fibrous composites. Since the mechanical properties of these samples were all very similar only one sample was chosen for detailed examination in the SEM (Sample #3). This sample resembled the LiAlO_2 sample #2 with definite fibrous nature to the microstructure and pore channels perpendicular to the fracture surface. The grain size appears much smaller in the Al_2O_3 than the #2 sample of LiAlO_2 . In Figure 1c and 3a one can see that the fibers have irregular cross-sections with a wide range of dimensions. There appears to be very good fiber-to-fiber bonding as seen in Figure 3a. Because of the wide range of fiber sizes and the irregular cross-sections, it is not instructive to think in terms of average sizes or strengths.

MECHANICAL TESTING

The "as-received" samples were checked for parallel faces and edges, and, if they were not satisfactory, they were hand lapped on 600 grit SiC until they were parallel to within the precision of hand-held calipers. The bulk densities were determined by measuring the samples accurately with the calipers and weighing them on a single pan electronic microbalance. Aluminum tabs were bonded to the samples using Duco cement which was thinned with acetone in order to infiltrate the cement into the composites under the grips. Without the infiltration, the shear strength of the composite was not high enough to cause shear transfer into the sample adequate to achieve a tensile failure in the gauge length of the specimen. A gauge length of 0.2" was used in all tests with a crosshead speed of 0.02" min. in the table model Instron. Pneumatic grips were used to grip the aluminum tabs. Alignment was accomplished with the aid of alignment marks on the tabs and the grips. It was assumed that the fibers

were aligned parallel to the sample edges. The samples were approximately 1/4" wide by approximately 1/8" thick.

In the case of the Al_2O_3 samples the strengths were so high that the samples could not be gripped adequately with cemented tabs and pneumatic grips. Either the tab/sample interface failed or the grip/tab interface sheared except in the case of sample #5. The first four specimens were all tested in tension to the stresses indicated, but gripping difficulties precluded tensile failure. These specimens were all tested in 4-pt, 1/3-pt bending with an outer span of 0.875" and an inner span of 0.292" with a crosshead speed of 0.02"/min. Acoustic emission from these samples was monitored by mounting the transducer to the end of the specimen.

The acoustic emission in the tensile tests was monitored by attaching the transducer to the lower tab and the rate of emission was monitored. The gate on the counter was adjusted to eliminate counts from the machine noises using an aluminum dummy specimen.

The results are presented as acoustic emission rate vs. time and load vs. time superimposed on the same chart. In some cases AE was not monitored because there was suspicion that the transducer was producing a slight bending moment on the specimen. However, as seen in Table 2, the use of the transducer produced no observable difference in the results.

RESULTS

The detailed results for the early lot of Al_2O_3 materials were reported earlier and will not be repeated here.

The strength results for the MgO samples are presented in Table 1. The strength values were clustered into two groups, thus the sample numbering sequence in the table. The fracture generally initiated near one edge and propagated more or less perpendicular to the sample edge. There were local deviations but in none of the tests did the crack propagate parallel to the fiber alignment for any detectable distance as one might expect for a loosely bonded bundle of fibers in which the severe flaw in each was randomly located in the gauge length. There was not widespread "pullout" of fibers. One expects the macroscopic crack to originate at the sample edge since the large pores (or cavities) create the largest stress concentration when open to the surface. Also, any slight parasitic bending moment would cause the highest stress at the edge.

The acoustic emission curves and load deflection curves are plotted in Figures 22-30 for the MgO samples. In several of these curves the slopes are very low at the beginning and increase with time becoming stiffer with strain. Figure 23 is an extreme example of this effect. In this case the aluminum tabs slipped in the pneumatic grip until the grips gouged the tab enough to support the shear stress buildup. In other cases, such as Figure 25, the shoulder on the curve results from random fractures (acoustic activity) thus decreasing the rigidity. But the increasing slope after the shoulder may result from rotation of misaligned fibers to the parallel orientation where they begin to contribute to the stiffness. Thus, although the early low-load increase in stiffness is probably an artifact of the gripping and testing procedure, the later increases after significant acoustic activity (perhaps from fracturing during fiber rotation) are

Table 1 Results of tensile tests on magnesia fiber composite samples ($\dot{\epsilon} = 0.1/\text{min}$)

Sample #	Density (g/cm ³)	Breaking Load (lb.)	Strength (psi)	Comments
1	1.45	9.1	286	AE settings too low
4	1.52	9.7	302	
6	1.39	10.3	292	
9	1.50	11.7	355	Broke near tab
11	1.39	9.1	296	Broke near tab
8	1.42	---	---	Broke near handling
2	1.52	2.6	104	
3	1.49	2.2	75	
5	1.15	2.9	107	Wrong setting on AE counter
7	1.36	3.3	123	
10	1.50	3.9	133	
12	1.12	3.8	124	

probably a real effect caused by the lack of "perfect" alignment in the original composites.

In general, for the weaker samples, measurable acoustic emission began at about one half of the ultimate strength. However, in the case of the stronger samples, acoustic emission began at 1/5 to 1/3 of the ultimate strength.

The strength and density data for the LiAlO_2 materials are tabulated in Table 2, and the load-deflection and acoustic emission curves are presented in Figures 31 - 37. There is again a grouping of strong samples and weak samples with the strong ones showing a general trend of strength increasing with density. There was a noticeable difference in the microstructure of the individual fibers or bundles between the strong and weak samples as described in the previous section. The stronger samples had much finer fibrils and perhaps a finer grain size although this latter point is not well-documented.

There was a major difference in the fracture path in these two sets of samples. In all of the strong samples but sample #9, the initial crack was arrested and deflected parallel to the fiber alignment causing delamination-type regions on the fracture surface. The crack then propagated across the fibers, and in some cases, became deflected

again forming sizeable steps on the fracture surface (see sketch).

Side view of Sample #5

Table 2 Results of tensile tests on LiAlO₂ fiber composite samples of ($\dot{\epsilon}$ = 0.1/min)

Sample #	Density (g/cm ³)	Breaking Load (lb)	Strength (psi)	Comments
1	1.49	25.8	713	
5	1.09	13.6	364	AE not recorded
6	1.12	20.8	460	
8	1.51	20.7	552	
9	1.32	26.7	686	AE not recorded
11	1.43	24.3	600	AE not recorded
2	1.41	3.0	81	Damaged when received
3	1.13	4.5	112	
4	1.25	2.1	56	AE not recorded
7	1.49	7.0	176	
10	1.45	4.3	211	
12	1.41	---	---	Broken when received

In the case of the weaker samples the fracture surface was more or less planar with local surface roughness. One would expect the latter when the properties tend toward isotropy and/or a major stress concentration initiates fracture. One would expect the former with fairly strong fibers and relatively weak bonding between fibers.

Using the micrographs from Figure 7d we've estimated the areal density of fibers in sample #2 to be $\sim 30,000/\text{in}^2$. With an average radius of 0.0019 in. the fibers have an average strength of ~ 260 psi. This value should be equal to the stress at fracture in the load bearing part of the cross-section of the sample which is just equal to the strength of the sample divided by the percentage of theoretical density when the sample is composed of a bundle of non-interacting rods. For sample #2 this latter calculation (using 40% of theoretical) yields 202 psi for the strength of the LiAlO_2 which compares favorably with 260 psi above for the average strength of the fibers.

The acoustic emission results for the LiAlO_2 samples are not very illuminating. In general, the stronger samples showed much more acoustic emission, which one would expect from the tortuous fracture path, than the weaker specimens.

The mechanical test results for the Al_2O_3 samples are presented in Table 3 and the acoustic emission and load-deflection curves presented in Figures 11-21. These strengths appear very high compared to the other materials. However, one must remember that these densities represent a range of 52.3% of theoretical (2.07 g/cm^3) to 62.4% of theoretical (2.47 g/cm^3) compared to 31% of the theoretical (1.12 g/cm^3) to 42% of theoretical (1.52 g/cm^3) for MgO . The LiAlO_2 densities are closer to those

Table 3 Results of 4-pt bending tests on alumina fiber composite samples (outer span 0.875", inner span 0.292", crosshead speed 0.02"/min)

Sample #	Density (g/cm ³)	Breaking Load (lbs)	Strength (psi)	Comments
1	2.24	18.8	4,946	Pretested to 1,738 psi in tension
2	2.35	17.5	3,628	2,175 in tension
3	2.10	14.5	4,215	1,469 in tension
4	2.20	20.8	5,415	2,325 in tension
5	2.07	51.0 (in tension)	1,440	tested in tension
6	2.33	14.5	3,907	
7	2.18	33.6	6,192	
8	2.22	43.0	5,823	
9	2.37	19.2	4,610	
10	2.17	18.8	4,739	
11	---	---	---	Broken in handling
12	2.47	24.6	5,809	
8 (early lot)	2.65	---	9,215	(no AE until failure)
9 (early lot)	2.65	---	9,348	

of MgO than those of Al₂O₃. (I do not have a theoretical density for LiAlO₂.) Also, the tensile tests put much larger effective volumes under stress than do the 4-pt bend tests. From the Weibull statistic we have that R, the risk of rupture, is given by

$$R = \int \left(\frac{\sigma}{\sigma_0} \right)^m dV = KV \left(\frac{\sigma_{\max}}{\sigma_0} \right)^m$$

where σ_0 is a normalizing constant, m is the Weibull modulus, K is the load factor, and $\sigma_{\max}$ is the maximum stress in volume, V , of the specimen. Assuming V is constant, $K=1$ for pure tension and the load factor for pure bending (as between the inner load points in 4-pt bend) is $K_{PB} = \frac{1}{2(m+1)}$. In the present case, the volume of the pure bend state is ~50% larger than the tensile test volume; but with a rather narrow strength distribution $m=6$ to 12 , the K_{PB} is very small compared to 1 . Thus, we expect the tensile strength to be considerably smaller than the bend strength. (Without more test data we cannot be more specific.) The actual relationship is

$$\frac{\sigma_{\text{tension}}}{\sigma_{\text{bend}}} = \left(\frac{K_{\text{bend}} V_{\text{bend}}}{K_{\text{tension}} V_{\text{tension}}} \right)^{1/m}$$

The relative values of tensile-proof stress and bending strengths suggest an m value on the order of $2-4$, a rather broad strength distribution.

From the acoustic emission curves, we see that significant emission starts as low as 15% of the ultimate load, suggesting local, random fiber breaks at quite low stresses.

The retest data of samples from the early Al_2O_3 lot are presented at the bottom of Table 3. Again, we see the very large strengths at this high density which is ~67% of the theoretical density (more on the σ_f vs. density relationship below).

DISCUSSION

The original objective of determining individual fiber strengths was frustrated by the lack of handleability of the individual fibers (or small bundles) that were first delivered to us. Perhaps if the shipping step were eliminated and a small horizontal whisker tester were used, strengths of individual fibers or bundles could be measured if extremely short gauge lengths were used. We found in our early tests the bundles tended to pull apart into individual (apparently short) fibrils. Because of these problems, we resorted to sintered specimens of aligned fibers.

The specimens of aligned fibers upon close examination in the SEM consisted of sintered clumps separated by fine (apparently 3-D) fibers in the case of the MgO . The alumina materials were also irregular in microstructures with a range of fiber sizes and shapes sintered together with misaligned fibers. In both of these cases it does not seem very useful to calculate "average" fiber strengths based on erroneous assumptions about the microstructure. In my January 17, 1980, letter report, I estimated the average stress in the alumina at the onset of significant acoustic activity assuming no stress concentrations but uniform load bearing by aligned rods of alumina. This calculation is nothing more than multiplying the appropriate apparent stress in the composite by the percentage of

theoretical density. If we do a similar estimate for MgO we arrive at much lower values for the onset of cracking because the strengths are lower at comparable densities. The same conclusion is true of LiAlO₂ in high strength samples because cracking started at lower percentages of the ultimate strength and in the weaker ones because they were much weaker than the Al₂O₃.

In low density fibrous composites of constant composition in which the bulk density is increased by compaction, the strength usually increases monotonically with density (see Sutor and Tressler, Am. Ceram. Soc. Bull. 55(12), 1055-58 (1976) and Meiser, Williamson and Tressler, Am. Ceram. Soc. Bull. 57 (8), 731-734 (1978)).

In the case of the Al₂O₃ materials, the most dense and clearly the strongest, the strength generally decreases with density except apparently at the lower end per the January 17, 1980, letter report. The data for LiAlO₂ and MgO are presented as tensile strength vs. density in Figure 10. The high strength group of LiAlO₂ tends to follow this general rule and perhaps the high strength group of MgO. But the lower strength groups do not follow this trend suggesting that some preparation parameter dominates the fiber strengths. It is also possible that damage incurred during shipping caused these low strengths since some of the specimen ends were broken. However, there were no noticeable breaks or defects in the ones tested. Some samples as noted were broken and fell apart in handling. Based on the microstructural observations for LiAlO₂ specimens, there may have been processing differences between the two groups of LiAlO₂.

Based on mechanical and microstructural considerations alone, the LiAlO₂ materials were the best at a given density.

Figure 1a.--Al₂O₃ (Sample #3), Mag 30x

Figure 1b.--Al₂O₃ (Sample #3), Mag 30x

Figure 1c.--Al₂O₃ (Sample #3), Mag 100x

Figure 1d.--Al₂O₃ (Sample #3) Mag 500x

Figure 2a.-- Al_2O_3 (Sample #3), Tilt + 10°, Mag 30x

Figure 2b.-- Al_2O_3 (Sample #3), Tilt +10°, Mag 100x

Figure 2c.-- Al_2O_3 (Sample #3) +10° Tilt, Mag 500x

Figure 2d.-- Al_2O_3 (Sample #3), -10° Tilt, Mag 30x

Figure 3a.--Al₂O₃ (Sample #3), -10° Tilt, Mag 100x

Figure 3b.--Al₂O₃ (Sample #3), -10 Tilt, Mag 500x

Figure 4a.--MgO (Sample #4), Mag 22x

Figure 4b.--MgO (Sample #4), Mag 22x

Figure 4c.--MgO (Sample #4) Mag 72x

Figure 4d.--MgO (Sample #4), Mag 720x

Figure 4e.--MgO (Sample #4), +10° Tilt, Mag 22x

Figure 4f.--MgO (Sample #4), +10° Tilt, Mag 71x

Figure 4g.--MgO (Sample #4), +10° Tilt Mag 710x

Figure 5a.--MgO (Sample #4), -10° Tilt, Mag 22x

Figure 5b.--MgO (Sample #4), -10° Tilt, Mag 71x

Figure 5c.--MgO (Sample #4), - 10° Tilt, Mag 710x

Figure 5d.--MgO (Sample #7), Mag 29x

Figure 5e.--MgO (Sample #7), Mag 97x

Figure 5f.--MgO (Sample #8), Mag 980x

Figure 6a.-- (Sample #7), + 10° Tilt, Mag 29x

Figure 6b.--MgO (Sample #7), +10° Tilt, Mag 98x

Figure 6c.--MgO (Sample #7), +10° Tilt, Mag 970x

Figure 6d.--MgO (Sample #7), -10° Tilt, Mag 29x

Figure 6e.--MgO (Sample #7), -10° Tilt, Mag 97x

Figure 6f.--MgO (Sample #7), -10° Tilt, Mag 970x

Figure 7a.--LiAlO₂ (Sample #2), Mag 27x

Figure 7b.--LiAlO₂ (Sample #2) Mag 910x

Figure 7c.--LiAlO₂ (Sample #2), +10° Tilt, Mag 28x

Figure 7d.--LiAlO₂ (Sample #2), +10° Tilt, Mag 92x

Figure 7e.--LiAlO₂ (Sample #2), +10° Tilt, Mag 920x

Figure 8a.--LiAlO₂ (Sample #2), -10° Tilt, Mag 28x

Figure 8b.--LiAlO₂ (Sample #2), -10° Tilt, Mag 93x

Figure 8c.--LiAlO₂ (Sample #2), -10° Tilt, Mag 920x

Figure 8d.--LiAlO₂ (Sample #6), Mag 29x

Figure 8e.--LiAlO₂ (Sample #6), Mag 98x

Figure 8f.--LiAlO₂ (Sample #6), Mag 980x

Figure 9a.--LiAlO₂ (Sample #6), + 10° Tilt, Mag 30x

Figure 9b.--LiAlO₂ (Sample #6), +10° Tilt, Mag 100x

Figure 9c.--LiAlO₂ (Sample #6), +10° Tilt, Mag 1000x

Figure 9d.--(Sample #6), +10° Tilt, Mag 100x

Figure 10.--Tensile Strength vs. Density for MgO
and LiAlO₂ Fiber Composites

Figure 11.--Al₂O₃ (Sample #1)

Figure 12.-- Al_2O_3 (Sample #2)

Figure 13.-- Al_2O_3 (Sample #3)

Figure 14.-- Al_2O_3 (Sample #4.)

Figure 15.--Al₂O₃ Tensile Test (Sample #5)

Figure 16.--Al₂O₃ (Sample #6)

Figure 17.-- Al_2O_3 (Sample #7)

Figure 18.--Al₂O₃ (Sample #8)

Figure 19. Al_2O_3 (Sample #9)

Figure 20. Al_2O_3 (Sample #10)

Figure 21.--Al₂O₃ (Sample #12)

Figure 22, --MgO (Sample #4)

Figure 23.--MgO (Sample #6)

Figure 24.--MgO (Sample #9)

Figure 25.--MgO (Sample #11)

Figure 26.--MgO (Sample #2)

Figure 27.--MgO (Sample #3)

Figure 28.--MgO (Sample #7)

Figure 29.--MgO (Sample #10)

Figure 30.--MgO (Sample #2)

Figure 31.--LiAlO₂ (Sample #1)

Figure 32.--LiAlO₂ (Sample #6)

Figure 33.--LiAlO₂ (Sample #4)

Figure 34.--LiAlO₂ (Sample #2)

Figure 35.--LiAlO₂ (Sample #3)

Figure 36.--LiAlO₂ (Sample #7)

Figure 37.--LiAlO₂ (Sample #10)