Development, Characterization and Evaluation of Materials for Open Cycle MHD

**Quarterly Report for the Period Ending
March 1977**

June 1977

**by
J. Lambert Bates,
Principal Investigator**

**Prepared for the Energy Research
and Development Administration
under Contract EY-76-C-06-1830**

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Energy Research and Development Administration.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.50
026-050	\$5.00
051-075	\$5.50
076-100	\$6.00
101-125	\$6.50
126-150	\$7.00
151-175	\$7.75
176-200	\$8.50
201-225	\$8.75
226-250	\$9.00
251-275	\$10.00
276-300	\$10.25

3 3679 00062 3332

BNWL-2004-6
UC-90g, 90c

DEVELOPMENT, CHARACTERIZATION, AND EVALUATION
OF MATERIALS FOR OPEN CYCLE MHD

Quarterly Report for the Period Ending
March 1977

June 1977

by
J. Lambert Bates, Principal Investigator

Prepared for the Energy Research
and Development Administration
under Contract EY-77-C-06-1830

Battelle
Pacific Northwest Laboratories
Richland, Washington 99352

CONTENTS

LIST OF FIGURES	ii
1.0 OBJECTIVES	1
2.0 SCOPE	1
3.0 TECHNICAL PROGRESS	
3.1 Electrochemical Effects of Alkali Seed on Electrodes and Insulators	1
3.1.1 Testing Procedures	2
3.1.2 Results	4
3.2 Electrode-Insulator Development	27
3.2.1 Electrode/Insulator/Leadout System for U.S. U-25 Channel	27
3.3 Post-Test Characterization of Electrodes and Insulators for U-02 Phase II	35
3.3.1 MgO Insulators	37
3.3.2 Current Leadouts	41
3.3.3 Electrodes	41
3.3.4 Summary and Conclusions	91
3.4 Characterization-Evaluation of MHD Materials	96
3.4.1 Thermal Diffusivity/Conductivity	97
4.0 WORK ANTICIPATED DURING NEXT QUARTER	101
4.1 Electrochemical Effects	101
4.2 Electrode-Insulator Development	101
4.3 Characterization and Evaluation	101
REFERENCES	102
DISTRIBUTION	

LIST OF FIGURES

1. Electrochemical Test Configuration 3	3
2. Electrochemical Test Configuration 4	5
3. Acicular Second Phase Formed in $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Due to Evaluation of Iron	9
4. $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ After Testing in SMF-10 Coal Slag .	11
5. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Control Sample After Testing in SMF-10 Coal Slag	11
6. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Anode After Testing in SMF-10 Coal Slag	12
7. Microstructures of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode After Testing in SMF-10 Coal Slag	12
8. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode After Testing in SMF-10 Coal Slag	13
9. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode After Testing in SMF-10 Coal Slag	14
10. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode After Testing in SMF-10 Coal Slag	15
11. $0.75\text{MgAl}_2\text{O}_3 \cdot 0.25\text{Fe}_3\text{O}_4$ Electrode Cathode After Testing in SA-1 Coal Slag	16
12. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode After Testing in SA-1 Coal Slag	18
13. $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode After Testing in SA-1 Coal Slag	20
14. $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode After Testing in K_2SO_4 at 1373K	21
15. Microstructure of Hot Pressed $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$	23
16. $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$ Electrodes After Testing in K_2SO_4	25
17. HfO_2 - CeO_2 - Y_2O_3 /La(Mg)CrO/Mo-Ti Composite Electrode Tested on K_2SO_4 without an Applied Field	28
18. Structure of Hot Pressed $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.8\text{Y}_2\text{O}_3$ /La _{0.95} Mg _{0.05} CrO ₃ Mo-Ti Composite Electrode	31

19.	Microstructure of Hot Pressed $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$ and $\text{La}_{0.95}\text{Mg}_{0.05}\text{C}_2\text{O}_3$ Composite	34
20.	Cross Sections of Electrode Pairs from U.S. Channel Tested in USSR U-02 Phase II	38
21.	Cross Sections of Electrode Pairs from U.S. Channel Tested in USSR U-02 Phase II	39
22.	Microstructures of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ Graded Cathode 1103 after 69 hrs at ~ 1 amps/cm ²	43
23.	Microstructure of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ Graded Cathode 1105 after 131 hrs with open circuit	44
24.	Microstructures of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$	45
25.	Microstructure of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ Graded Anode 2103 after 69 hrs at ~ 1 amp/cm ²	47
26.	Microstructure of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ Graded Anode 2105 after 131 hrs with Open Circuit	48
27.	Microstructure of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ Cathode 1315 after 19 hrs with Current Density 0.9 amps/cm ² and 36 hrs with Current Density ~ 0.5 amps/cm ²	50
28.	Microstructures of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ Cathode 1315 Sharing	51
29.	Microstructure of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ Anode 2315 after 19 hrs with Current Density of ~ 0.9 amps/cm ² and 36 hrs with Current Density ~ 0.5 amps/cm ²	53
30.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1416 after 131 hrs with Open Current	54
31.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1417 after 25 hrs at ~ 1.1 amps/cm ²	55
32.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1417 after 17 hrs with Current Density of ~ 0.9 amp/cm ² Anode 2419	56
33.	Microstructural Cross Section of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1416	59
34.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1416 near Plasma Surface	60
35.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1416	60

36.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1416 . . .	62
37.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1416 . . .	62
38.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1419 . . .	63
39.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$	64
40.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Anode 2416 after 131 Hours with Open Circuit	66
41.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Anode 2417 after 24 Hours with Current Density of 1.1 amps/cm ²	67
42.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Anode 2419 after 18 Hours with Current Density of ~0.9 amps/cm ²	68
43.	Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Anode 2416 Cross Section	69
44.	Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1524 after 75 Hours at 1.1 amps/cm ²	71
45.	Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Anode 2524 after 75 Hours at ~1.1 amps/cm ²	72
46.	Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1524 Cross Section	74
47.	Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1524 . . .	76
48.	Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Cathode 1524 . . .	77
49.	Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ Anode 2524 . . .	79
50.	Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ Cathode 1627 after 61.5 Hours at ~1 amps/cm ²	81
51.	Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ Anode 2627 after 61.5 Hours at ~1.1 amps/cm ²	82
52.	Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ Cathode 1630 after 75 Hours at ~0.2 amps/cm ²	83
53.	Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ Anode 2630 after 75 Hours at ~0.2 amps/cm ²	84
54.	Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_2$ Cathode 1627 Showing Lanthanum Oxide Formation and Chromium Loss from Surface .	86

55. Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ Cathode 1627	87
56. Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ Cathode 1627	89
57. Thermal Diffusivity of Plasma Sprayed $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$	97
58. Thermal Diffusivity of Hot Pressed $0.82\text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.10\text{Y}_2\text{O}_3$	99
59. Thermal Conductivity of Hot Pressed $0.82\text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.10\text{Y}_2\text{O}_3$	100

1.0 OBJECTIVES

The objectives of this program are to develop, test, characterize, and evaluate materials for open-cycle, coal-fired MHD power generators. The specific immediate goals emphasize electrode and insulator materials, including: 1) testing and evaluation of the enhanced effects of alkali seed on materials in a dc electric field; 2) development and testing of improved electrodes and insulators with controlled microstructures, compositions and properties; and 3) characterization and evaluation of materials relating to both the US MHD Program and the US-USSR Cooperative Program for MHD power generators.

2.0 SCOPE

The scope of this program encompasses the following areas:

- Reproducible laboratory testing of both ceramic and metal electrode materials and insulator materials in alkali seed/slag under dc electric current and voltages as functions of temperature, seed/slag, and composition.
- Development and fabrication of electrodes, insulators, and other related materials with controlled electrical, chemical, and physical properties, including evaluation in laboratory tests in US MHD test facilities and as part of the US-USSR testing program.
- Characterization and evaluation of materials tested under the US-USSR and the US MHD programs include the measurement and analysis of structural, chemical, and thermophysical properties of electrodes, insulators, slag, and other related materials before and after testing.

3.0 TECHNICAL PROGRESS

3.1 Electrochemical Effects of Alkali Seed on Electrodes and Insulators

Alkali metal seed and high direct electric currents pose two severe synergistic conditions for electrodes and insulators in the channels of open-cycle, fossil-fueled MHD power generators. Recent long-term tests of materials, ⁽¹⁻⁴⁾ have shown that potassium penetration and reaction can be extensive in both electrodes and insulators and that the presence of a dc

electric field can substantially enhance these effects. The degree of penetration and reaction varies from material to material and is dependent upon the composition, structure and fabrication. External factors, such as the state of the seed, either as gas, liquid, solid or dissolved in slag, temperature, and the electric current density and voltage influence these effects.

Engineering-type laboratory tests are being developed and testing has been initiated for evaluating potential electrodes and insulators⁽²⁾ in the presence of potassium seed/slag in an applied dc electric field and current. The preliminary test procedures and initial results have been described previously.⁽²⁾ Test procedures are being improved, materials tested initially are being tested and evaluated more intensively, and preliminary testing of other electrode materials has been initiated.

3.1.1 Testing Procedures

The test procedures and equipment were modified over those used previously⁽²⁾ [configurations 1 and 2]: 1) to reduce electrolyte migration along the sample current leadout, which short-circuit the current through the electrolyte coating, and 2) to provide independent testing in air with current flow without slag or seed present. This latter provides a base for evaluating the effects of direct current on structure independent of slag or seed.

3.1.1.1 Test Configuration 3

Test configuration 3 was developed to reduce the possibility of electrolyte migration and current flow along the sample surface from the electrolyte bath to the platinum current leadout, which also holds the sample. In some tests, an electrolyte was deposited on the electrode above the level of the liquid bath and short circuited the current to the platinum wire current leadout, partially bypassing the electrode material. To minimize this effect, a closed end cylindrical tube with an internal electrode is used as a sample (test configuration 3, Figure 1). The base of the cavity in the cylinder is coated with platinum paste and dried. A platinum wire (0.013 cm diameter) is placed in contact with the platinum paste into the base area providing a mechanically tight fit between the leadout and the sample. The

FIGURE 1. Electrochemical test configuration 3

platinum leadout is constrained from pulling away from the platinum paste and wire assemblage by looping the current leadout wire through an alumina pin set in holes in the cylinder. The second leadout is connected to the platinum crucible resulting in current transport through the electrolyte between the crucible and the electrode. The assembly is then suspended to the desired depth in the molten electrolyte at temperature.

The current density is calculated using the surface area of the cylinder in contact with the electrolyte.

3.1.1.2 Test Configuration 4

A reference is required when comparing the electrochemical effects when seed or seed/slag are present during the passage of current. These data bases are provided by independently testing the electrode in a dc field without the presence of either electrolyte or slag (configuration 4, Figure 2). Platinum leadout wires are attached to the ends of a sample bar, and during testing at temperature, current flows through the sample between the platinum leadouts. The current density is calculated using the average cross sectional area of the electrode.

3.1.2 Results

Testing of $\text{La}(\text{Mg})\text{CrO}_3$ and $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ spinel electrode materials in molten K_2SO_4 has continued and has been extended to testing in simulated coal slags containing potassium. Testing has involved configurations 1, 2, 3 and 4⁽²⁾ from 1373 to 1776°K in both molten potassium sulfate and slag/seed. These tests are summarized in Table 1.

The reagent grade potassium sulfate (K_2SO_4) electrolyte is premelted in the test crucible. The color, after melting, is slightly yellow. After testing with the lathanium chromites, the K_2SO_4 color is yellow, suggesting some solution of chromium in the molten salt. There is no change in color after testing of MAFF-31.

It is anticipated that the composition of coal slags, especially the Fe, K and Ca content, will strongly influence the electrochemical effects of electrode and insulator materials.

TEST CONFIGURATION 4

FIGURE 2. Electrochemical test configuration 4

Table 1. SUMMARY OF ELECTROCHEMICAL TESTS

Test No.	Sample	Electrolyte	Temperature °K	Time Min.	Current Density, amp/cm ²	Comments
5	Hf-1, Hf-2, Hf-3 (82mole%HfO ₂ +10mole% CeO ₂ +8mole%Y ₂ O ₃)	K ₂ SO ₄	1373	280	2.04 anode 2.03 cathode	Test conf. 2 cathode erosion> anode (both missing to level of electrolyte)
7	S-121 (25mole%Fe ₃ O ₄ + 75mole%MgAl ₂ O ₄)	Slag SMF-10	1673	177	1.09 anode 1.31 cathode	Test conf. 2 anode erosion> cathode erosion
8	S-121 (25mole%Fe ₃ O ₄ + 75mole%MgAl ₂ O ₄)	Slag SMF-10	-	-	-	Test conf. 1
10	S-121-H (25mole%Fe ₃ O ₄ + 75mole%MgAl ₂ O ₄)	Slag SMF-10	1673	418	1.22 cathode	Test conf. 1 cathode missing to level of slag
11	S-63-A (25mole%Fe ₃ O ₄ + 75mole%MgAl ₂ O ₄)	Slag SA-1	1773	180	0.209 cathode	Test conf. 3 cathode missing to level of slag
12	S-53-A (25mole%Fe ₃ O ₄ + 75mole%MgAl ₂ O ₄)	Slag SA-2	1374 1474	300 120	0.18 cathode	Test conf. 13 sample intact with some erosion
13	S-53-B (25mole%Fe ₃ O ₄ + 75mole%MgAl ₂ O ₄)	Slag SK-615	1473	300	0.1	Test conf. 3 still conducting at termination
18	EP-HFL-1A (82mole%HfO ₂ -8mole% Y ₂ O ₃ -10CeO ₂ +5mole% MgO-95mole%LaCrO ₃ + 50mole%Mo-0.05mole%Ti)	K ₂ SO ₄	1373	300	no current	Mo-Ti oxidized chromite severely reacted HfO ₂ minimal reaction
19	121X (25mole%Fe ₃ O ₄ + 75mole%MgAl ₂ O ₄)	none	1373	4440 to 6900	1	Test conf. 4 no potassium

The slag compositions were selected to represent the Montana "Rosebud" and Illinois "6" type coals. The SMF-10 represents that typical of Montana (Rosebud) Colstrip and was obtained from a conventional Montana power steam plant, being a mixture of both fly ash and bottom ash. The high potassium content (11.47 wt.% compared to 0.43 wt.% of the original slag) is by doping with potassium carbonate.⁽⁵⁾ Slag SA-1 is synthetic iron-free SMF-10. The synthetic SK-615 is a slag representing a high iron containing eastern coal similar to Illinois 6 and is similar to a NBS reference coal slag K-615. The compositions of these slag electrolytes are summarized in Table 2. Included in the table are two general parameters used to describe slags. Both of these ratios are relative ratios and do not precisely describe the relative corrosive-erosive behavior of a slag toward a refractory.

Table 2. Composition of Coal Slags (wt.%)

	<u>SMF-10</u>	<u>SA-1</u>	<u>SK-615</u>
SiO ₂	41.69	45	47.6
Al ₂ O ₃	18.22	20	19.7
Fe ₂ O ₃	4.38		20.5
MgO	5.62	6	0.9
CaO	17.93	20	7.9
Na ₂ O	0.35		
K ₂ O	11.37	9	2.6
TiO ₂	0.75		0.8
P ₂ O ₅	0.30		
Base/acid ratio*	0.65	0.54	0.47
Silica ratio**	60	64	62

$$*B/A = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3 + TiO_2}$$

$$**Si = \frac{SiO_2 \times 100}{SiO_2 + Fe_2O_3 + CaO + MgO}$$

3.1.2.1 $0.65\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$

The $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ spinel (MAFF-31) was fabricated using sintering methods similar to that used in the U-02 Phase II test in the USSR.⁽²⁾ The nominal density was 3.61 g/cm^3 (~90% TD). The resultant large grain structure contains impurities of Ca and Si which are concentrated at the grain boundaries along with the iron. Otherwise, the MAFF-31 was single phase.

The MAFF-31 degrades in molten K_2SO_4 , reacting with the K_2SO_4 above 1100°K with enhanced degradation occurring when an electric potential and flow of direct electric current is present.

The reactions with the molten K_2SO_4 appear to be initiated at the grain boundaries as the sulfate apparently reacts with the Ca-Si-Fe second phase.

An acicular second phase, depleted in magnesium with a concentration in iron and aluminum, forms in the large MAFF-31 grains. This phase contains potassium but no sulfur whereas the gross grain boundary reaction associated with the grain boundaries and impurities contain both potassium and sulfur. Further decomposition of the MAFF-31 can occur, resulting in areas of nearly pure iron oxide but free of potassium. These areas are surrounded by an iron depleted matrix enriched in Mg and Al with potassium present.

Reaction which results in the exsolution of the iron and second phase formation in the MAFF-31 appears to be initiated near the grain boundaries. Occasionally deposits containing mixed oxides of Mg and Fe are found on the exterior surfaces of the test samples (Figure 3). In areas of these deposits, these surface deposits are free of potassium and seed penetration along the grain boundaries is reduced.

The $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ does not appear to be thermally or electrically stable. Using configuration 4, a MAFF-31 bar (121X) was suspended 4400-6900 minutes at 1373°K in air without either seed or slag present (Test No. 14). A current density of 1 amp/cm^2 was applied across the sample. The outward appearance of the MAFF-31 remained unchanged. However, a second phase was found throughout the sample, with a concentration near the outside surface (Figure 3). No differences were observed between the anode and cathode ends of the sample. Although an analysis of this phase has not been completed, it appears to be similar to phases observed in other MAFF-31

electrode tests in air of the Mg-Fe-Al-O system where exsolution of iron is observed.⁽⁶⁾ Phase equilibrium would predict the second phase to be Fe_2O_3 .⁽⁷⁾ Cooling of the MAFF-31 below 1400°C in air should lead to the formation of Fe_2O_3 . Two forms of Fe_2O_3 can form: 1) gamma, which remains in the spinel lattice with the formation of iron vacancies, and 2) alpha which must be exsolved from the spinel matrix. Formation of gamma Fe_2O_3 has little effect on the electrical conductivity as opposed to alpha Fe_2O_3 which can lower the conductivity both by forming regions of lower electrically conductive Fe_2O_3 and by lowering the iron content of the remaining spinel.

FIGURE 3. Acicular second phase formed in $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ due to exsolution of iron.

During most of the test, the electric potential required to keep the current density at 1 amp/cm^2 gradually increased from 4.5 to 12.6 volts. Over the last few hours of the test the voltage increased rapidly to 50 volts (the capacity of the power supply) after which the current density decreased to less than 0.1 amp/cm^2 . Although the formation of the second phase could be the cause of the increase in voltage, it most probably was due to an increased contact resistance between the platinum and the electrode. The platinum paste on the anode at the end of the test had degraded with a poor electrical conductance. The platinum paste on the cathode remained

*The test terminated due to open circuit conditions after 4400 minutes and before 6900 minutes, and time was not recorded.

a good conductor. The low conductivity of the anode platinum paste could have led to an increase in the electric potential and eventually to an open circuit which occurred between 4400 and 6900 minutes. The platinum wire leadouts retained a high conductance.

Even without potassium, the initial single phase material decomposes at 1373°K in the 10's of hours to at least two phases. This decomposition is enhanced by an electric potential with an applied electric field and current resulting in significant decreases in the electrical conductivity.

Testing of the $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ in a potassium containing slag was also initiated (Tests 7, 10-13, Table 1). These results are summarized in detail.

Test No. 7. The MAFF-31 was tested in configuration 2 in SMF-10 slag with current densities between 1.1 and 1.3 amps/cm² for 177 hours. Although both the anode and cathode were lowered once to maintain electrical continuity, the test was terminated after 177 hours when open circuits were observed (Figure 4).

Based on the electrical conductivity of the spinel and coal slag, the electric potential required for a current of 0.1 amps to flow through the slag and electrode was calculated to be 21.6 volts. The voltage across the anodes and cathodes was calculated to be 3.2 and 2.5 volts, respectively. The total measured potential ranged from 16 at the beginning of the test to 30.5 at the end. During the test, cyclic electric potential fluctuations of ± 0.6 volts were observed. This cycle consisted of a major fluctuation lasting up to 1 second then a constant potential for 2 to 6 seconds, minor fluctuations for 1 second, then the major fluctuation. These fluctuations in the electric potential were not observed in K_2SO_4 electrolyte experiments. The fluctuations may be due to polarization of the slag leading to electrolysis, however, the experiment is not designed to allow observation of electrolysis. Polarization and electrolysis can cause major changes in the local composition of the slag and the furnace atmosphere around the anode and cathode. The microstructure of the control is shown in Figure 5. Slag has penetrated the open porosity and into some grain boundaries near the surface (Figure 5a). Each of the grains close to the tip is surrounded by a

ANODE CATHODE CONTROL

FIGURE 4. $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ after testing in SMF-10 coal slag (Test No. 7).

a

0.2 cm

b

0.01 cm

FIGURE 5. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ control sample after testing in SMF-10 coal slag (Test No. 7).

FIGURE 6. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ anode after testing in SMF-10 coal slag (Test No. 7).

FIGURE 7. Microstructures of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode after testing in SMF-10 coal slag (Test No. 7).

second phase (perhaps slag) (Figure 5b). No evidence of second phase growth from the boundaries into the grains, as observed in similar tests using K_2SO_4 , were observed.

The microstructure of the anode remained essentially unchanged from the untested sample except for deposits at the grain boundaries and in some of the pores (Figure 6). The tip of the anode had recessed to above the electrolyte level prior to test termination; consequently, microstructural changes due to the dissolution may not be present. The tip showed considerable penetration of the slag along the grain boundaries and into some pores. Otherwise, the microstructure appears unchanged with no deposits seen on the tip surface.

Gross microstructural changes occurred in the cathode, (Figure 7). The microstructure of the cathode tip is similar to the original MAFF-31 (Figure 7a). Increased porosity is found in both the neck and tip area (Figure 7b). At least six different phases can be seen in the tip including slag penetration (Figure 8). Slag penetration is also observed along the grain boundaries in the sample above the original slag level (Figure 9). A deposit is also found along the surface of the cathode immediately above the level of the electrolyte. Some slag penetration is observed in this area.

0.02 cm

FIGURE 8. Microstructure of $0.75MgAl_2O_4 \cdot 0.25Fe_3O_4$ cathode after testing in SMF-10 coal slag (Test No. 7)

FIGURE 9. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode after testing in SMF-10 coal slag (Test No. 7).

Test No. 10. The MAFF-31 was tested as cathode (configuration 1) in SMF-10 coal slag with a constant current density of 1.22 amps/cm^2 . The electric potential remained constant at 3.5 volts during the first 250 minutes of the test, then increased to 20.5 volts after 418 minutes when the test was terminated. The bottom 7.5 mm of the cathode had reacted with the slag. The tip of the remaining cathode underwent extensive microstructural change, (Figure 10). The cathode is porous immediately above the tip and slag has penetrated through the grain boundaries. No evidence of iron exsolution or second phase formation, i.e., the acicular second phase, was observed.

FIGURE 10. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode after testing in SMF-10 coal slag (Test No. 10).

FIGURE 11. $0.75\text{MgAl}_2\text{O}_3 \cdot 0.25\text{Fe}_3\text{O}_4$ electrode cathode after testing in SA-1 coal slag (Test No.12) (a) exterior, (b) cross section; compare with anode (Figure 13).

Test No. 11. The $0.75 \text{ MgAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ was tested in cylindrical sample configuration 3 in slag SA-1. The electrical potential to maintain 0.1 amps (0.21 amps/cm^2 based on uniform conduction through the cylinder walls immersed in the slag) increased from 1.5 to 5.5 volts during the 180 minute test. The test was terminated when an open circuit developed.

The slag had penetrated the MAFF-31 through the grain boundaries, eventually filling the cavity of the cylinder and contacting the platinum electrode. No exsolution of iron or second phases were formed in the spinel, as was found in those tests performed in K_2SO_4 or without an electrolyte.

Test No. 12. The MAFF-31 was again tested in configuration 3 for two different thermal and electrical cycles in low iron slag SA-1. Initially, the cylinder was heated to 1373°K for 300 minutes with a constant direct current voltage of 46 volts. During this time, the current decreased from 0.1 to 0.02 amps/cm^2 . Only 3 mm of the cylinder was in contact with the slag. For the second cycle, the cylinder with some residual slag attached was heated to 1673°K and inserted again into the slag, then cooled to 1473°K for testing in an applied field of 0.1 volts and 0.02 amps/cm^2 . After 120 minutes the electric potential was removed and the temperature increased to 1673°K before the sample was removed. The assembly was then cooled to ambient temperature. The lower portion of the electrode is coated with slag (Figure 11) and the MAFF-31 region at the bottom in contact with the slag is severely eroded at the grain boundaries with a second phase (Figure 12a). Some slag is found on the interior surfaces of the electrode. This second phase is not observed in the upper areas of the sample near the top level of the slag (Figure 12c). In this region the grains are surrounded by the slag and another granular second phase is concentrated more along the grain boundaries than the interior of the grains. Above the slag level, a thin reactive layer is found on the exterior surface (Figure 12b). However, penetration along the grain boundaries occurred near the sample surface.

a

0.01 cm

b

c

0.02 cm

FIGURE 12. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode after testing in SA-1 coal slag (Test No. 12).

Test No. 13. The $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ was again tested at 1473°K in configuration 3, but with slag SK-615 which has a higher iron and lower calcium content than the SA-1 slag used in Test 12. The sample was inserted into the slag to a depth of 3 mm, or a little below the bottom of the interior hole of the cylinder. Consequently, the current flow is primarily through the base of the sample and not the side walls. The test was terminated after 300 minutes but the system was still conducting an average current of 0.3 amps/cm^2 .

The electrode experienced only minimum reaction and degradation compared with the severe reactions for the same spinel in Tests 7 and 12 (Figure 13). Some microstructural changes did occur near the surface at the bottom of the cylinder resulting in decreased porosity and the formation of a second phase. The width of this microstructural change is $\sim 0.3 \text{ mm}$. The remainder of the sample remained unchanged, although there is some evidence of a second phase reaction at the grain boundary near the slag-cathode interface.

Test No. 15. For comparison, a $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ hollow cylinder cathode was tested in configuration 3 at 1373°K with molten K_2SO_4 as the electrolyte. The current density was 0.3 amps/cm^2 and the test was terminated after 240 minutes with current still flowing. The sample swelled in the area submersed in the K_2SO_4 $\sim 5 \text{ mm}$ (Figure 14). The grain boundaries were severely attacked by the K_2SO_4 forming a second phase. This separation at the boundaries resulted in a general breakup of the sample. In addition potassium sulfate deposited on the inside of the cylinder.

Degradation of the grain boundaries apparently occurs as the K_2SO_4 reacts with the Ca-Si-Fe second phase formed at the grain boundaries during fabrication.

The following preliminary conclusions can be made concerning the electrochemical behavior of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ in K_2SO_4 /coal slag. However, they are subject to further change as the evaluation of these and other samples are completed.

a

0.2cm

b

0.2cm

FIGURE 13. $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode after testing in SA-1 coal slag (Test No. 12), (a) exterior, (b) cross section; compare with cathode (Figure 11).

a

0.2cm

b

FIGURE 14. $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode after testing in K_2SO_4 at 1373°K (Test No. 15).

- The $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ appears to be unstable in air when a direct current and voltage are applied. Exsolution of the iron occurs, resulting in the formation of a number of second phases including high aluminum-iron-rich phases. This instability is consistent with the phase equilibria data.
- The $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ is severely attacked by molten K_2SO_4 , especially in a dc electric field. The reactions occur initially at the grain boundaries, where the K_2SO_4 reacts with the Ca-Si rich second phase present in the as-fabricated MAFF-31. Subsequent decomposition is enhanced by the presence of K_2SO_4 and the direct electric current where the potassium concentrates in an aluminum and iron rich phase.
- The electrochemical reactions of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ with coal slag containing potassium appears to be dependent upon the slag composition. The reactions are much more severe in slags containing only small amounts of iron. However, in a slag containing ~20 wt.% iron, the electrochemical reactions are minimal. Decomposition second phase formation and exsolution of iron in the slags with a dc current are not observed.

3.1.2.2 $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$

The $\text{HfO}_2 \cdot \text{CeO}_2 \cdot \text{Y}_2\text{O}_3$ system is being considered as a potential electrode for open cycle MHD. HfO_2 has a higher monoclinic to tetragonal phase transformation temperature than ZrO_2 and can be stabilized in a cubic structure with oxides such as Y_2O_3 and CaO . Samples of hot pressed $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$ were prepared by Argonne National Laboratory. The oxide was hot pressed at 1673°K for 80 minutes with a pressure of 3.17×10^6 pascals (4600 psi) in a graphite die to a density of 8.16 g/cm^3 (~89% TD). The resultant structure was 75% monoclinic, 25% fcc Y_2O_3 stabilized HfO_2 , and 2% fcc CeO_2 . The compact was composed of larger monoclinic HfO_2 grains surrounded by a small grained matrix of Y_2O_3 , CeO_2 , and Y_2O_3 stabilized HfO_2 (Figure 15). The $\text{HfO}_2 \cdot \text{Y}_2\text{O}_3 \cdot \text{CeO}_2$ material is composed

0.01 cm

0.02 cm

FIGURE 15. Microstructure of hot pressed $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$.

of large dense grains of HfO_2 , essentially free of $\text{Y}_2\text{O}_3 \cdot \text{CeO}_2$.^{*} Some of the smaller HfO_2 grains are porous and contain yttria. Very little chemical reaction between the yttria and ceria occurred during hot pressing since yttria is not found in the ceria grains or yttria in the ceria. No ceria is found with the HfO_2 . The major impurities are zirconia and silica.

The zirconia is from the initial hafnia powder which initially contained 5.4 mole% zirconia. The silica content of the initial hafnia powder was 0.4 mole% and additional silica was probably picked up during powder processing. The silica is associated mostly with the large hafnia grains.

Test No. 5. The hafnia-ceria-yttria sample was tested in configuration 2 in K_2SO_4 at 1373°K for 280 minutes with current densities near 2 amps/cm². The cathode and anode had reacted and eroded above the level of the K_2SO_4 electrolyte, eventually resulting in an open circuit when the cathode failed. The cathode had separated from the Pt current leadout and fell into the electrolyte.

During the test, the electrolyte migrated along the electrode surface to the platinum wire. Evidence of this migration is indicated by an increase in current for a constant applied voltage during the test. However, the migrated K_2SO_4 did not totally short circuit the hafnia as evidenced by the enhanced reaction.

The control sample remained relatively unaffected (Figure 16.) Potassium did not penetrate either the grains or the grain boundaries. Examination of the hafnia and yttria grains by SEM-EDAX showed no evidence of potassium attack. Ceria particles were not found on the surface, but the ceria in the interior, not exposed to the surface, was unreacted.

The anodes and cathodes reacted with the K_2SO_4 vapor above the liquid level of the electrolyte (Figure 16). In the unreacted zones for both anode and cathode (below the level of the electrolyte), only trace amounts

^{*}The microstructural features were analyzed using SEM-EDXRA with the compositions determined using a Tracor Northern analyzer which provides wt.% compositions accurate to $\pm 3\%$ with detectable limits of 0.1 wt.% for elements with atomic weight above sodium. Oxygen was determined by difference assuming carbides, borides and nitrides are not present. Some difficulty with the oxygen difference calculations are found with high concentrations of hafnium and/or magnesium which is now being resolved. The results of the preliminary analysis is given in Table 2. (The oxygen calculations are not given in this table.)

FIGURE 16. $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$ electrodes after testing in K_2SO_4 (Test No. 5); (a) anode, (b) cathode, and (c) control.

of potassium were found and the microstructure appeared to be the same as the original starting oxide. No K_2SO_4 deposits were found on the surface, however, the sample had been washed with water prior to mounting, removing all water soluble deposits.

The cathode above the liquid K_2SO_4 level had reacted resulting in major microstructural changes (Figure 16). Many of the large monoclinic HfO_2 grains separated into smaller grains. The smaller grains contain mostly Ce, Hf, and Y (the analyses are tabulated in Table 3), while the larger grains are mostly HfO_2 . Multiphase deposits are also found on the outside surfaces of the reacted portion of the cathode. The phases of nearly pure Hf and Hf-K compounds make up these deposits along with some platinum metal. Another deposit has a similar phase plus a compound which could be $KCeHfO_4$. A similar analogous compound, potassium-cerium-zirconate, has been observed in laboratory tests⁽⁸⁾ and in MHD tests (U.S. Phase I test in the U.S.S.R. U-02).⁽¹⁾ This compound was not found in either the control or anode samples of this test.

The anode exhibited an increase in porosity in the reacted zone above the K_2SO_4 level (Figure 16). This porosity apparently resulted as the yttria and ceria phases were removed from around the larger HfO_2 grains. No potassium was found in this area. The anode was not washed like the cathode, consequently no water soluble compound could have been removed. However, small amounts of potassium were found in the open pores of the anode submersed in the K_2SO_4 . A deposit of yttria has formed on the surface of the anode submersed in the electrolyte. The yttria contains some CeO_2 . No evidence of yttria loss from adjacent areas of the anode itself was observed.

The sample appeared to contain substantial silicon in the HfO_2 oxide of the original electrodes. It did not migrate appreciably during the test nor was it associated with potassium. Aluminum from an unknown source is also dispersed throughout the sample.

The complex microstructure and phases in the Hf-Ce-Y oxide make it difficult for examination. However, the electro-chemical effects are complex and further testing and evaluation will prove valuable.

Test No. 18. The sample* for Test 18 was a four-layered structure:
1) 80 mole% HfO_2 , 8 mole% CeO_2 , 12 mole% Y_2O_3 ; 2) $\text{La}(\text{Mg})\text{CrO}_3$ with 5 mole% MgO (General Refractories Powder); 3) mixture of $\text{La}(\text{Mg})\text{CrO}_3$ and Mo/Ti alloy, (50 wt% Mo); and 4) Mo/Ti alloy, (see Section 3.2.1). The layer thicknesses are 0.05 cm, 0.3 cm, 0.15-0.1 cm and 0.05 cm, respectively. The overall density of the hot pressed sample averaged 94.5% of theoretical.

A sample was immersed in molten K_2SO_4 at 1373°K for 300 minutes without an applied electric potential (Figure 17). The Mo/Ti alloy and most of the Mo/Ti alloy- LaCrO_3 composite had oxidized above the K_2SO_4 level. The LaCrO_3 had severely reacted with the electrolyte. The band in the chromite corresponds closely to the level of the electrolyte. The hafnia layer exhibited no evidence of interaction with the seed.

3.2 Electrode-Insulator Development

3.2.1 Electrode/Insulator/Leadout System for US U-25 Channel.

A program of electrode/insulator/leadout development was initiated to identify a hot electrode system for the US U-25 channel to be tested in the USSR. This effort was conducted in cooperation with other laboratories and facilities in the United States on a priority basis. The major goal was to investigate the potential for fabricating a ceramic electrode system utilizing hot pressing techniques. The development effort was aimed toward:

- (1) The development of a quality electrode/insulator/leadout system fabricated in a one-step process such as hot pressing.
- (2) The evaluation of the potential of a commercial supplier to fabricate these systems for the U-25 channel using continuous hot pressing techniques.
- (3) The testing of some prototype systems prepared by hot pressing in the MIT test facility.

*Hot pressed by Eagle-Picher Industries, Miami, Oklahoma.

A. $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$

B. $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$

C. K_2SO_4

FIGURE 17. $\text{HfO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3/\text{La}(\text{Mg})\text{CrO}_2/\text{Mo-Ti}$ composite electrode tested on K_2SO_4 without an applied field.

This effort was restricted by the abbreviated schedule requested by ERDA and the need to involve a commercial organization with the potential capabilities for fabricating the required large number of electrode systems for the U-25 channel within the proposed time schedule.

The electrode/insulator/leadout systems to be investigated included a refractory ceramic electrode with:

- (1) A good electrical conductivity at lower temperatures.

- (2) A high temperature electrically conductive protective oxide surface (cap) which is thermally and chemically stable to the MHD plasma.
- (3) A graded structure containing a metal cermet at the cold surface which can be bonded/brazed to the copper window frame. The choice of materials was based upon preliminary data available at the time. These materials include:

- (a) La(Mg)CrO_3 and $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ (MAFF-31) were chosen as the highly conducting electrode materials.
- (b) HfO_2 stabilized with Y_2O_3 and CeO_2 and Y_2O_3 stabilized ZrO_2 were selected as the refractory protective surfaces.
- (c) Ti-Mo and Fe-Mo were selected as the current leadout metals.

The combination of materials was selected because of the need for materials with closely matching thermal expansions. The choice of a metal for the current leadout was also further limited because of the need for a high melting point to complement high hot pressing temperatures.

Preliminary work to hot press electrode materials was conducted by Eagle-Picher Industries of Miami, Oklahoma, using a continuous hot pressing process. This effort subsequently was continued to select the best fabrication procedures to fabricate a number of electrode/insulator/leadout systems for possible testing at MIT. Three systems were selected initially for development:

- (1) Hot pressed ceramic-metal composite with a $\text{HfO}_2(\text{CeO}_2 \cdot \text{Y}_2\text{O}_3)$ surface graded into a MAFF-31 spinel, graded into a titanium metal back.
- (2) Hot pressed ceramic-metal composite with a $\text{HfO}_2(\text{CeO}_2 \cdot \text{Y}_2\text{O}_3)$ surface graded into a La(Mg)CrO_3 electrode, graded into a titanium metal back.
- (3) Hot pressed ceramic-metal composite with a $0.12\text{Y}_2\text{O}_3 \cdot 0.88\text{ZrO}_2$ surface graded into a La(Mg)CrO_2 electrode, graded into a titanium back.

3.2.1.1 Development Results

The use of titanium metal for the electrode leadout allowed fabrication temperatures as high as 1550°C. These produced densities of ~95% TD for the MAFF-31 and ~91% TD for the $\text{La}(\text{Mg})\text{CrO}_3$ using either ZrO_2 or HfO_2 caps. The densities of the caps were >97% TD. However, intermediate delamination occurred between the electrode and the surface caps and especially between the electrode and the titanium. In addition, the titanium appeared to react with the $\text{La}(\text{Mg})\text{CrO}_3$ and MAFF-31. Cracks perpendicular to the layers also occurred intermittently, apparently because of these chemical reactions.

A 50-50 wt% mixture of Mo-Ti was subsequently selected for further study. The Mo-Ti exhibited complete solid solubility in all proportions above 883°C and the liquidus is also higher than the melting point of pure titanium. This allowed the fabrication temperature to be increased. The coefficient of thermal expansion of this alloy appears to be matched to that of MAFF-31 and $\text{La}(\text{Mg})\text{CrO}_3$, with titanium slightly higher and molybdenum slightly lower. Preliminary evaluations indicated a significant reduction in delamination and cracking of the electrode using Mo-Ti (Figure 18.) Whether this was due to increased ceramic density and strength, because of the higher fabrication temperatures, the reduced reaction between the metal and the electrode, or an improved ceramic metal bond has yet to be determined.

3.2.1.2 Fabrication

Hot pressing was conducted using graphite dies in an argon atmosphere. Both rectangular, 1.02 cm (0.400 in) X 3.49 cm (1.375 in) and circular, 4.13 cm (1.625 in) diameter dies were used. Pressures from 2.81×10^6 to $3.87 \times 10^6 \text{ Kg/m}^2$ (4000 to 5500 psi) were employed with pressing times from 10 to 60 minutes. Temperatures varied between 1300 and 1700°C. The following materials were used:

- $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$, -325 mesh sinterable powder.
- $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$, low temperature calcined, -325 mesh with ultimate crystallite size 3-4 μm .

FIGURE 18. Structure of hot pressed $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3 / \text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3\text{Mo-Ti}$ composite electrode

- $0.80\text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.12\text{Y}_2\text{O}_3$, an admixture of -325 mesh powders.
- $0.12\text{Y}_2\text{O}_3 \cdot 0.88\text{ZrO}_2$, fully stabilized sinterable powder.
- Titanium-molybdenum, a 50-50 wt% admixture of -325 mesh Ti and -200 mesh Mo, >99% purity.

3.2.1.3 $0.08\text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.12\text{Y}_2\text{O}_3$ Cap MAFF-31. Samples were hot pressed in rectangular dies at 1350 to 1700°C and pressures from 2.75×10^7 to 3.79×10^7 Pascals (4000-5500 psi) for 10 to 60 minutes. Those pressed at lower temperatures appeared to produce the better quality electrodes. The higher temperatures appeared to increase the delamination and resulted in precipitation of some metal near the MAFF-31 and HfO_2 interface.

The final electrode consisted of a 0.127 cm thick HfO_2 surface cap, a 0.305 cm thick MAFF-31 spinel electrode, with a transition layer of 50-50 MAFF-31/Mo-Ti and a pure Mo/Ti layer. The overall electrode thickness was 0.571 cm and the overall bulk density was ~93% TD, with very high density HfO_2 . The top and bottom surfaces were ground to a finished thickness of 0.453 cm, which included a ~0.05 cm thick layer of HfO_2 . The sides and ends of the electrodes were ground to the final electrode dimensions. This grinding revealed delaminations within the MAFF-31/Mo-Ti graded layer and between this layer and the pure metal.

$0.80 \text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.12\text{Y}_2\text{O}_3$ Cap on $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$. These electrodes were pressed in the circular dies between 1450-1750°C and 2.81×10^6 to $3.87 \times 10^6 \text{ Kg/m}^2$ (4000-5500 psi). The overall bulk densities averaged ~94.5% TD. Circular dies were used because an interaction between the $\text{La}(\text{Mg})\text{CrO}_3$ and graphite die walls of the rectangular dies. Because of the narrow die width, 1.02 cm (0.400 inches), this reaction complicated the removal of the sample due to stresses encountered in breaking the bonds between the tooling and the sample. The breakage occurred perpendicular to the layers rather than as interlayer delaminations.

The cylindrical dies were loaded so that the final dimensions would include a 0.127cm (0.05 in) thick HfO_2 cap, a 0.305cm (0.120 in) of chromite, 50-50 $\text{La}(\text{Mg})\text{CrO}_3$ /Mo-Ti transition layer, and a pure Mo-Ti metal layer of ~0.14cm (0.055 in) thick. The circular pieces were cut and

ground into rectangular sections, 0.953 cm (0.375 in) wide, and as long as possible. The electrodes were ground to thickness of 0.45 cm (0.180 in) with the refractory cap ~ 0.05 cm thick. The ground sections appeared to be free of laminations or crazing.

$0.12\text{Y}_2\text{O}_3 \cdot 0.88\text{ZrO}_2$ Cap on $\text{La}(\text{Mg})\text{CrO}_3$. These electrodes were fabricated by the same procedures used to prepare the previous HfO_2 -MAFF-31 electrodes. The results were similar relative to density. Delamination was not a problem although crazing of the Y_2O_3 stabilized ZrO_2 was observed. Crazing was also observed to occur progressively, spreading on a freshly pressed sample over 10-20 minutes period. This may be related to the larger mismatch in thermal expansion between the ZrO_2 -chromite than the HfO_2 -chromite. However, the cap did remain in place even after grounding.

The electrodes are now being evaluated relative to microstructure, thermal treatment and thermomechanical resistance. If the results are positive, the electrodes will be brazed or bonded to copper electrodes and MgAl_2O_4 insulators will be arc plasma sprayed on the sides. If successful, the finished electrode/insulator/leadout will then be tested in the MIT facility.

A $0.80\text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.12\text{Y}_2\text{O}_3$ capped $\text{La}(\text{Mg})\text{CrO}_3$ layered electrode was hot pressed without a metal composite leadout. This structure was hot pressed at 1600°C and bonded very well, with densities very near theoretical (Figure 19). The presence of a metallic phase (presumed at this time to be Cr) at the interface indicates some evidence of reaction or reduction. The HfO_2 appears to be two phase as does the $\text{La}(\text{Mg})\text{CrO}_3$ near the interface. The $\text{La}(\text{Mg})\text{CrO}_3$ is very near theoretical density, compared to the much lower density when the Mo/Ti metal is present.

0.2 cm

1. $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$

2. $\text{La}(\text{Mg})\text{CrO}_3$

0.02 cm

0.01 cm

FIGURE 19. Microstructure of hot pressed $0.82\text{HfO}_2 \cdot 0.10\text{CeO}_2 \cdot 0.08\text{Y}_2\text{O}_3$ and $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_2\text{O}_3$ composite.

3.3 Post Characterization of Electrodes and Insulators for U-02 Phase II

Phase II testing of a US channel in the USSR U-02 MHD generator was completed in September 1976.⁽¹⁻²⁾ The test consisted of US channel electrode walls with USSR insulator walls.* The following electrode materials were tested in the Phase II channel:

- Graded $\text{CeO}_2\text{-ZrO}_2$ (35m%-78m% CeO_2)
- $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$
- $0.7\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$
- $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$
- $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ and $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$

The electrode materials⁽²⁾ were arranged in six modules pairs (Table 3) each consisting of five electrodes separated with MgO insulators. The side insulators were 90% TD MgO with 85% TD MgO as base insulators. Three different current leadouts-attachments⁽³⁾ were used: (1) Fired Platinum metallized with platinum paste, (2) Inconel with sprayed Inconel and Nicro braze 210, and (3) Copper screen with Cu-Ag BT brazes (Table 3). The metal screens were bonded to both the electrode and adjacent base MgO insulator.

The opposing electrode pairs were operated in open circuit, short circuit, or induced dc electric current modes for 75 hours under actual MHD conditions. The total test time was 131 hours including an approximate 10 hours startup and 36 hours pretesting at temperature and 10 hours shutdown. The plasma temperature averaged 2600°K and electrode surface temperatures approached 1950°K. Of the 30 electrode pairs nine retained their electrical continuity to the end of the test, eight pairs failed before or near the initiation of electric current under MHD conditions and the other remaining 14 failed during the test.

The channel was disassembled after the test, visually examined, and within an hour the electrode walls were placed in plastic bags containing a dry, inert gas with a drying agent. After returning to the US, the electrode walls were again examined and cast, as a unit, in an epoxy resin at the National Bureau of Standards (NBS). They were cut longitudinally into three slices on each side of the center line. An inside slice from

*Channel designed and fabricated by Westinghouse Research Laboratory, Pittsburgh, PA.

Table 3. ELECTRODE CURRENT LEAD OUTS PHASE II

Electrode Designation	Current Lead-Out		Electrode/Insulator Assembly		Electrode Material
	Screen	Wire	Metallization	Bonding	
1101 2101	Platinum	4-Platinum	Fired-on Pt	Fired-on Pt	Graded $\text{CeO}_2\text{-ZrO}_2$
1102 2102	"	2-Platinum	"	"	"
1103 2103	"	"	"	"	"
1104 2104	"	"	"	"	"
1105 2105	"	"	"	"	"
1206 2206	Inconel	1-Inconel	Sprayed Inconel	Microbraz 210	"
1207 2207	"	"	"	"	"
1208 2208	"	"	"	"	"
1209 2209	"	"	"	"	"
1210 2210	"	"	"	"	"
1311 2311	Platinum	4-Platinum	Fired-on Pt	Fired-on Pt	0.5 $\text{CeO}_2\text{-0.5 ZrO}_2$
1312 2312	"	2-Platinum	"	"	"
1213 2313	"	"	"	"	"
1314 2314	"	"	"	"	"
1315 2315	"	"	"	"	"
1416 2416	Copper	1-Copper	Sprayed Cu	BT Braze	0.75Mg $\text{Al}_2\text{O}_3\text{-0.25Fe}_3\text{O}_4$
1417 2417	"	"	"	"	"
1418 2418	Platinum	2-Platinum	Fired-on Pt	Fired-on Pt	"
1419 2419	"	"	"	"	"
1420 2420	Copper	1-Copper	Sprayed Cu	BT Braze	"
1521 2521	Platinum	4-Platinum	Fired-on Pt	Fired-on Pt	"
1522 2522	"	2-Platinum	"	"	"
1523 2523	Copper	1-Copper	Sprayed Cu	BT Braze	0.75 $\text{FeAl}_2\text{O}_3\text{-0.25Fe}_3\text{O}_4$
1524 2524	"	"	"	"	"
1525 2525	"	"	"	"	"
1626 2626	Copper	1-Copper	Sprayed Cu	BT Braze	LaCrO_3
1627 2627	"	"	"	"	"
1628 2628	"	"	"	"	"
1629 2629	Platinum	2-Platinum	Fired-on Pt	Fired-on Pt	"
1630 2630	Copper	1-Copper	Sprayed Cu	BT Braze	"

both the anode and cathode wall was supplied to the USSR specialists, a middle slice was provided to Battelle, Pacific Northwest Laboratories, (PNL) and an outside slice given to Westinghouse Research Laboratory (W). The remaining slices were retained at NBS.

The sections supplied to PNL were separated into the individual modules, photographed, (Figures 20 and 21) then separated into separate electrodes. These were ultrasonically cleaned in alcohol, again vacuum impregnated using a fluid resin* at 80°C to allow complete filling of all small cracks, cavities and pores. The cut surfaces of the electrode which were nearest the center-line of the electrode wall were ground without water and polished in a nonaqueous media using diamond polishing agents. The electrodes were examined metallographically and photographed. The polished cross sections were again ultrasonically cleaned in a volatile organic solvent, then coated prior to examination with the scanning electron microscope and electron microprobe.

The compositions were determined quantitatively from the electron microprobe using a Tracor Northern analyzer which provides weight percent compositions accurate to $\pm 3\%$ with detectable limits of 0.1 wt% for elements with atomic weights of 11 or above. Some difficulties were encountered in Na and Mg analysis and their accuracies are less. The results are given in weight percent, with oxygen being given as the difference, assuming minimal carbide, boride or nitride compounds are present.

The electrodes chosen for primary metallography, SEM and EDAX examination were those which operated with the highest current densities for the longest periods of time.

3.3.1 MgO Insulators

3.3.1.1 Fracture

The side MgO insulators (90% TD) which separated the electrodes were more extensively fractured than the base insulators (85% TD). Fracture of the side electrodes generally occurred adjacent the bottom of the electrodes with cracks running parallel to the electrode surface. The enhanced fracture may be related to the larger thermal gradients in the side insulators.

*Acme 655 with 555 catalyst

FIGURE 20. Cross sections of electrode pairs from U.S. channel tested in U.S.S.R. U-02 Phase II (2XXX and 1XXX electrodes are anodes and cathodes, respectively).

FIGURE 21. Cross sections of electrode pairs from U.S. channel tested in U.S.S.R. U-02. Phase II (2XXX and 1XXX electrodes are anodes and cathodes, respectively).

The base insulators were thermally shielded by the electrodes, which in some instances had separated from the insulators, thereby tempering thermal shock effects.

Fracture and degradation of the base MgO insulators occurred where potassium seed either penetrated the insulator (e.g., electrodes 1416, 1315, and 1522) or reacted with the brazing metal (e.g., electrodes 1206-1210). In all cases these effects were more severe on the cathode wall.

3.3.1.2 Reactions

The MgO reacted in varying degrees with all of the electrode materials. These interactions were greatest nearer the high temperature plasma surface. Reactions were most severe with the hercynite-magnetite ($0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$) and magnesium aluminum iron ($0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$) spinels, especially in those electrodes where evidence of electrode melting and/or flow occurred. Iron from these spinels diffused extensively into the side insulators, especially near the interface, and also iron diffused into the base insulators.

The reaction between the MgO and the $\text{CeO}_2 \cdot \text{ZrO}_2$ base electrodes was localized, resulting in multiphase structures in the contact area near the plasma surface. The La(Mg)CrO_3 reactions with the MgO were only slightly greater than that of the $\text{CeO}_2 \cdot \text{ZrO}_2$ electrodes, also at the plasma surface.

The La(Mg)CrO_3 electrodes and side insulators were often contaminated with the upstream hercynite-magnetite spinel which apparently melted and was carried by the gas stream over the MgO-chromite electrode surfaces. In these cases, especially on the cathode, the spinel completely covered the MgO insulator.

Potassium seed penetration was greater in the cathode insulators than in the anode insulators. Greater penetration and reaction occurred in the MgO associated with those electrodes which had the highest current densities for the longest times. Potassium penetrated the bottom MgO insulators and below the electrode-current leadout-insulator interfaces. The potassium did not react with the MgO, but generally deposited as carbonate in the open pores and cracks. The seed had reacted with the metal bonding in electrodes with high current densities for long times.

3.3.1.3 Microstructural Changes

The top MgO surfaces exposed to the high temperature plasma underwent extensive microstructural changes to depths between 0.2-0.4 cm. In those electrodes which fractured and were lost during the test and/or where the electrodes eroded significantly, restructuring was more extensive. This was apparently due to increased exposure to the high temperature plasma.

3.3.2 Current Leadouts

The metal current leadouts, in many cases, separated from the electrode or from both the electrode and the insulator. Separation was greatest on the cathodes. All the Inconel leadouts on the $\text{CeO}_2\cdot\text{ZrO}_2$ graded electrodes separated and reacted with the MgO, especially with the cathodes. Very little difference could be observed between the Pt and Cu current leadouts.

3.3.3 Electrodes

Many of the $\text{CeO}_2\cdot\text{ZrO}_2$ base cathodes were lost during the test, exposing the MgO insulation to the plasma. None of the anodes were lost, although most had separated from the MgO. The loss of these cathodes can possibly be attributed to a combination of factors:

- 1) Separation of the metal current leadout from the base of the electrode.
- 2) Fracture of side insulators and resultant loss of retaining capacity.
- 3) Unknown factors associated only with the cathode, e.g., electrochemical, seed and metal-current leadout effects.
- 4) The electrodes were relatively thin resulting in a high back surface temperature.

The $\text{CeO}_2\cdot\text{ZrO}_2$ cathodes and anodes were free of potassium, with no evidence of seed interaction to form the potassium cerium zirconate phases observed extensively in the corresponding electrodes of the Phase I test.⁽⁴⁻⁶⁾ This is apparently related to the higher operating temperatures of the electrodes as evidenced by the microstructural changes throughout the entire ceramic electrode.

In contrast, the iron-aluminum-magnetite, magnesium-aluminum-iron spinel and lanthanum chromite electrodes all remained intact although the side insulators had fractured and some current-outs separated from the electrodes.

Substantially thicker electrodes may have been a factor in holding the electrodes in place.

The reaction of the spinels with the MgO insulators was extensive. Reactions with the MgO near the plasma surface resulted in apparent melting and/or plastic flow by the gas stream. This often resulted in the formation of MgO rich caps which covered adjacent electrode surfaces. The apparent melting of the hercynite-magnetite electrodes and subsequent reaction with MgO resulted in gross surface contamination and some reaction with the downstream La(Mg)CrO_3 electrodes and insulators. The above reactions were significantly more severe in the cathodes than in the anodes.

The high temperature surfaces of all the electrodes were contaminated with calcium stabilized zirconium oxide, presumably from the U-02 combustor. The downstream electrode surfaces also were contaminated with $\text{CeO}_2 \cdot \text{ZrO}_2$ from the upstream electrodes.

3.3.3.1 $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ Graded Electrodes

Cathodes [1101-1105; 1206-1210]. Only six of the ten cathodes remained intact during the test. Of these, only 1103 and 1105 had retained an electrical continuity during the test allowing current to flow (Figures 22 and 23). All of the Inconel current leadouts separated from the cathodes and reacted with the MgO, but little reaction occurred with the $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ electrodes. The platinum current leadouts separated from the cathodes which were lost. However, the platinum remained attached to the MgO base insulator. The thickness of the cathodes had not changed during the test. The cathodes, which remained, fractured ~0.2-0.25 cm from the bottom of the cathode with the cracks extending the entire width of the electrode parallel to the surface. This corresponds approximately with the boundary between the $0.75\text{CeO}_2 \cdot 0.20\text{ZrO}_2 \cdot 0.02\text{Ta}_2\text{O}_5$ graded compositions.

The cathodes appear to be single phase, although a metal phase was found at some grain boundaries scattered throughout the bottom two-thirds of cathode 1103. Only minor amounts of potassium were present.

The top edge of the electrode had reacted with the adjacent MgO insulator (Figure 24d). In addition, the electrode had eroded where the

FIGURE 22. Microstructures of $\text{CeO}_2\cdot\text{ZrO}_2\cdot\text{Ta}_2\text{O}_5$ graded cathode 1103 after 69 hours at $\sim 1 \text{ amp/cm}^2$ (see Figure 25 for corresponding anode).

FIGURE 23. Microstructure of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ graded cathode 1105 after 131 hours operating with open circuit (see Figure 26 for corresponding anode).

a

b

c

d

0.01 cm

FIGURE 24. Microstructures of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$; (a) plasma surface, (b) below plasma surface, (c) near metal current lead-out, (d) electrode MgO interaction.

MgO insulator had been lost, forming a two phase structure in the area of interaction.

The electrode surfaces which were directly exposed to the plasma underwent extensive microstructural change to depths of up to 0.25 cm. For cathode 1103 (Figure 23) this occurred on the sides as well as on the top electrode surfaces because of the apparent loss of the MgO side insulators. This 0.08 cm thick, dense surface was recrystallized electrode material containing many large spherical pores (Figure 24a). Immediately below this the pores became irregular and elongated (~ 0.2 cm long) with their length parallel to the top surface (Figure 24b). The microstructure of the remaining electrodes also had been modified. Above the crack, the original large, dense grains could not be resolved.

Near the metal current leadout, restructuring resulted in the formation of equiaxed grains, ~ 0.003 cm in diameter, with extensive porosity and separation at the grain boundaries (Figure 24c).

The extensive restructuring possibly could be related to the separation of the electrodes from the MgO therein creating a thermal barrier, allowing the entire electrode to become hotter than expected. Evidence of separation during the test and not during shutdown is evidenced by the buildup of a porous material between the bottom of the electrode and the base insulator (Figure 22).

Anode [2101-2105; 2206-2210]. All of the graded $\text{CeO}_2 \cdot \text{ZrO}_2$ anodes remained relatively intact although the surfaces were eroded and the thickness of the anodes were reduced from the original 0.7 cm to 0.55 cm (Figures 25 and 26). The MgO side insulators were also eroded to depths significantly below the anode surfaces, especially those adjacent to the 2101-2105 anodes. The MgO also reacted with the anodes near the plasma surfaces.

The platinum current leadouts partially separated from the electrode and/or insulators. The Inconel leadouts also separated, generally from the anode and not the insulator. The separation from the cathode was more severe than from the anode. The reaction of the MgO with the Inconel of the anodes was significantly less than with the cathodes.

FIGURE 25. Microstructure of $\text{CeO}_2 \cdot \text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$ graded anode 2103 after 69 hours at $\sim 1 \text{ amp/cm}^2$ (see Figure 22 for corresponding cathode).

FIGURE 26. Microstructure of CeO₂·ZrO₂·Ta₂O₅ graded anode 2105 after 131 hours with open circuit (see Figure 23 for corresponding cathode).

The anodes also cracked ~0.2 to 0.25 cm from the bottom although the fracture was less severe than that observed in the cathodes. The electrode restructured, especially in the top 0.4 cm. The top 0.1 cm recrystallized, forming large grains with tear-like or spherical pores within the large grains. These pores became more irregular as the distance from the top surface increased. Like the cathode, most of the anode underwent microstructural changes. Only near the bottom could the original microstructure be resolved.

All of the anodes appeared to be single phase and were free of potassium with microstructures similar to the cathodes.

3.3.3.2 0.5 CeO₂•0.5 ZrO₂.

Cathodes [1311-1315]. The 1315 cathode was one of two which remained attached to the electrode wall during the test (Figure 27). The cathode thickness was approximately the same as that of the original electrodes. The platinum leadouts remained partially attached to the electrode but none remained attached to the MgO. There was a wide gap between the electrode and the bottom insulator which apparently occurred during the test since there was a buildup of a porous material in the area between the electrode and insulators. This material partially filled the void area and attached itself to both the electrode and MgO. This material was a two-phase porous structure of a MgO•CeO₂•ZrO₂ composition and also contained platinum and some potassium area (Figure 28c).

The entire electrode microstructure has been modified (Figure 28a). A few randomly oriented small cracks criss-crossed the restructured cathode. The top 0.03 cm was very dense with only a few pores at the grain boundaries. The central 0.2 cm contained columnar type pores, ~0.005 cm long, which reduced in size and number as the distance from the top surface increased.

The cathode had reacted slightly with the MgO in the few places it contacted the MgO side insulators. The sides of the electrode not in contact with the MgO were porous and with some erosion, suggesting the MgO was exposed directly to the plasma during the test.

The 0.5 CeO₂•0.5ZrO₂ is single phase except in the insulator-electrode reaction area.

FIGURE 27. Microstructure of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ cathode 1315 after 19 hours with current density $\sim 0.9 \text{ amp/cm}^2$ and 36 hours with current density $\sim 0.5 \text{ amp/cm}^2$ (see Figure 29 for corresponding anode).

a

0.05 cm

b

c

0.01 cm

FIGURE 28. Microstructures of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ cathode 1315 sharing; (a) recrystallized area b, (c) two phase structure between cathode and MgO (see Figure 27).

FIGURE 32. Microstructure of $0.75\text{MgAl}_2\text{O}_3 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1417 after 17 hours with current density of $\sim 0.9 \text{ amp/cm}^2$ (see Figure 40 for corresponding anode 2419).

Anodes [2311-2315]. All of the anodes remained intact during the test (Figure 29). The current leadouts separated from the MgO but remained attached to the anodes. Although the separation between the anode and base insulator was as wide as that for the cathode, the restructuring was less, suggesting possible electrochemical effects and not thermal effects. The surfaces of the anodes had eroded slightly and the thicknesses were the same as before the test.

The anodes were relatively free of cracks and although some modification of the microstructure occurred near the exposed surfaces, some of the residual microstructure could be resolved. Recrystallization at the top surface and edges occurred to depth of ~ 0.08 cm, resulting in a structure of dense large grain oxide containing spherical pores. The trailing edge of the electrode top surface had the appearance of melting and/or plastic flow.

The $0.5 \text{ CeO}_2 \cdot 0.5 \text{ ZrO}_2$ was single phase except in localized areas of insulator-electrode reaction near the plasma surface. There was no interaction or material buildup in the gap between the anode and MgO like that observed for the cathode.

3.3.3.3 $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$

Cathodes 1416-1420, 1521-1523 and Anodes 2416-2420, 2521-2528. The performance of the $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathodes fabricated at PNL and Trans Tech (1419) was the same within the limits of evaluation (Figures 30-32). The cathodes exhibited extensive degradation, erosion, and reaction with the MgO near the plasma surface. This included recession of from 0.3 to 0.4 cm from an original height of 1.3 cm. The recession of cathode 1417 was very large, ~ 0.9 cm (Figure 31). All of the spinel cathodes reacted extensively with the MgO side insulators to depths as great as 0.56 cm from the recessed, eroded surface. The surfaces showed evidences of melting and/or material flow, and recrystallization occurred to depths of up to 0.5 cm.

The metal current leadouts, both copper and platinum, were completely or partly separated from the cathode. The penetration and deposition of

FIGURE 29. Microstructure of $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ anode 2315 after 19 hours with current density of $\sim 0.9 \text{ amp/cm}^2$ and 36 hours with current density $\sim 0.5 \text{ amp/cm}^2$ (see Figure 27 for corresponding cathode).

FIGURE 30. Microstructure of $0.75\text{MgAl}_2\text{O}_3 \cdot 0.24\text{Fe}_3\text{O}_4$ cathode 1416 after 131 hours with open circuit (see Figure 32 for corresponding anode 2416).

FIGURE 31. Microstructure of $0.75\text{MgAl}_2\text{O}_3 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1417 after 25 hours at $\sim 1.1 \text{ amps/cm}^2$ (see Figure 41 for corresponding anode 2412).

potassium seed was extensive through the cracks and open porosity of the MgO insulation for those cathodes which operated at the higher current density for any period of time. Concentration of seed was greatest near the area of the cathode-base insulators and metal current leadout. The remainder of the cathode which had not recrystallized exhibited extensive fracture along the boundaries of the large grains. This is attributed to reaction of potassium with Si and Ca impurities present in the grain boundaries after fabrication.

The recrystallized areas underwent extensive microstructural and compositional changes. The microstructural changes were greater in those electrodes which operated at the highest current densities and for the longest times.

The electrodes near the plasma surfaces were depleted in iron, partially in magnesium and enriched in aluminum. This resulted in the formation of MgAl_2O_4 with only small amounts of iron. These surfaces often contained ZrO_2 (with some CaO).

Some parts of the cathode surfaces were covered with MgO from adjacent insulators and contaminated with Ca-stabilized ZrO_2 (from the combustor) and CeO_2 (from upstream electrodes). In some portions of the cathode surfaces, ~ 0.01 cm, the surface was entirely MgO with a ZrO_2 second phase. The presence of this covering may have influenced the decomposition of the original iron spinel into various iron rich and iron depleted phases. This combination of MgO, MgAl_2O_3 , Al_2O_3 , and ZrO_2 was probably the whitish surface observed on the electrode surfaces at the termination of the test.

The restructured portion of the $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ underwent multiphase compositional changes. The makeup and distribution of these phases were complex, with up to three different phases in some portions of the recrystallized area. In general, there was a compositional change into iron rich and iron depleted phases which contain different amounts of aluminum and magnesium. Seed was localized in the areas of high aluminum and in grain boundary areas which originally contained high Ca and Si.

To illustrate the complex compositions and phases found in the Mg-Al-Fe spinel cathodes, two examples are discussed in detail.

Cathode 1416. The top surface was dense, large grains with large pores immediately below the surface (Figures 33,34). The matrix of this near surface was depleted in Fe(1.9%) with increased Al(30.3%) plus Mg(8.3%) and O(57.4%), as compared to a nominal starting composition of Mg(10%), Fe(28%), Al(21%) and O(40%) (Figure 34a). This phase also contained impurities of Si, Zr, Ca, La and 0.2%K, presumably impurities from upstream components. The second phase was Ca stabilized ZrO_2 with 2.9% Ce and smaller amounts of Mg, Fe and 0.3%K. There was also a very small second phase of Mg(40.6%) and Fe(4.0%) with minor amounts of Al, Si and Ca. This structure was found to depths of ~ 0.05 - 0.07 cm below the surface.

Immediately below this layer was a two to three phase region with a brick-like fracture pattern which extends to varied depths within the cathode (Figure 33). The concentration of this cross-hatch pattern was continuous to a depth of ~ 0.3 - 0.4 cm from the surface, then decreased and, at ~ 0.6 cm, was gone. This structure contained three phases of about the same volume concentration. The apparent continuous matrix contained Mg(39.7%), Al(1.4%), Fe(19.9%), and O(38.4%) with minor amounts of Si and Zr. It was in this area that the brick-like cracking occurred. The other phase which was darker and rounded in shape was Mg(11.9%), Al(31.9%), Fe(6.1%) and O(48.5%), with some Si, La, Ce and 0.1%K. Surrounding each of the latter darker phase was a thin layer rich in iron (34.6%) with Mg(13.1%), Al(13.7%), and O(37.2%).

Gradually replacing this phase, beginning ~ 0.3 cm from the surface, was another structure which exhibited an increase in porosity (Figure 35c). The matrix of this structure was similar in composition to the darker major phase described above, but higher in Al and depleted in Fe. The amounts of each phase varied as the distance changed. A nearly continuous lighter second (~ 15 - 20% of the area) was free of Al and contained Mg(27.3%), Fe(39.6%) and O(32.2%) with 0.1%K and 0.5% Si. This second phase had its highest concentration ~ 0.5 cm from top cathode surface.

The cathode was fractured across its width, ~ 0.6 cm from the surface. The matrix near this crack contained Mg(7.8%), Al(18.6%), Fe(32.6%), Ca(5%) and O(34.6%) (Figure 35d). A second phase of Mg(3.9%), Al(28.9%), Fe(15.0%), K(6.5%), and O(44.7%) was also concentrated near this crack.

PLASMA SURFACE

MgO INSULATOR

0.05 cm

FIGURE 33. Microstructural cross section of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1416 (See Figure 30).

FIGURE 34. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1416 near plasma surface (see Figure 33).

Figure 35. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1416; (c) 3.6 mm and (d) 7.5 mm from plasma surface (see Figure 33).

At approximately 0.7 cm below the top surface the composition and structure was near that of the original cathode, but with grain boundary cracking (Figure 36). There was a high concentration of potassium at these cracks which increased rapidly toward the Pt current leadout. The potassium reaction at the grain boundaries apparently is due to the presence of impurities of Ca and Si formed during the fabrication processes (Figure 37). This could have provided the mechanism for potassium penetration into the bulk spinel and possibly influenced the exsolution of iron and the formation of other phases in the spinel.

Cathode 1419. This cathode exhibited similar microstructural changes to that of 1416 except to a lesser degree (Figures 32 and 38). However, an MgO cap had formed over the electrode surface, apparently resulting as the upstream electrodes reacted with the MgO insulators and subsequently flowed over the downstream cathodes.

The plasma surface was mostly MgO with some iron, Mg(54.6%), Fe(3.8%) and O(41.4%). This 0.012 cm thick layer also contained the Ca stabilized ZrO_2 second phase.

At 0.01 cm, the iron spinel phase began as a two-phase structure with a matrix still rich in Mg(50.4%), depleted in Al(0.9%) and Fe(15.9%) with O(30.7%) (Figure 39a). The second phase more closely resembled that of the starting iron spinel with Mg(13.3%), Fe(28.1%), Al(19.6%), and O(38.5%). This phase continued to a depth of ~ 0.2 to 0.25 cm and was associated with the brick-like cracking pattern (Figure 39b).

This phase gradually changed, with the latter phase becoming the most prominent (Figure 38). At 0.25 cm, the cathode contained large rounded pores with a second phase of Mg(12.7%), Al(12.1%), Fe(37.3%), and O(35.7%). Some Ca, Si and K also were associated with this phase (Figure 39c).

A localized area of iron oxide (Fe_2O_3) free of Mg and Al was located near an internal fracture, ~ 3.0 mm from the plasma surface (Figure 39d). This phase contained stringers thought to be FeO and is surrounded by an area of Fe depleted spinel.

e

0.02 cm

FIGURE 36. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1416 (e) 8.5 mm from plasma surface.

f

0.02 cm

FIGURE 37. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1416 (f) 11 mm from plasma surface.

FIGURE 38. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1419 (see Figure 32).

A

B

C

0.01 cm

D

FIGURE 39. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$; (a) 0.1 mm, (b) 2 mm, (c) 2.5 mm, and (d) ~ 3.0 mm, respectively from plasma surface.

The general conditions of the anodes were similar to that of the cathodes but to a lesser degree (Figures 40-42). Recession of the anodes was ~0.35 cm, essentially the same as the cathodes. The anodes reacted less with the MgO than the cathodes, only to depths of approximately 0.4 cm, and the top surface recrystallized from 0.2 to 0.4 cm below the recessed surface. The anodes showed less evidence of surface melting or plastic flow, and the MgO did not cover the anode to the extent observed on the cathodes. Some metal current leadouts had separated and the MgO was relatively free of potassium.

The spinel of the anodes, like the cathodes which had not recrystallized, exhibited extensive fracture along the grain boundaries. The restructured parts of the anodes also exhibited extensive multiphase compositional changes. These changes were complex and are summarized in the following examples:

Anode 2416. The anode had reacted with the MgO insulator near the plasma surface (Figures 40 and 43). The Cu current leadout separated from the spinel electrode, but remained attached to the base MgO insulator. The anode eroded 0.3 to 0.4 cm, with the top surface showing possible evidence of melting, flow, and breakup. The top 0.2 cm had recrystallized (Figure 43a). Below the recrystallization, the anode fractured along the boundaries of the large grains.

The top exposed surface was primarily MgAl_2O_4 with excess oxygen but free of iron (<1%) (Figure 43a). A second phase of Ca stabilized ZrO_2 was found in localized areas within 0.02 cm of the surface. This layer of iron free anode was ~0.065 cm thick. At 0.065 cm, both Fe and K were observed in a matrix of Mg(9.6%), Al(26.4%) and Fe(17%) spinel but depleted in Fe and Mg (Figure 43b). The second phase was a potassium aluminum silicate with Fe(2%), Al(10.9%), Si(19.9%), Zr(1.7%), Ca(1.2%), K(14.1%), and O(49.6%).

At 0.17 cm from the surface in the recrystallized area, the anode retained the original composition, but contained a second phase of Si and Ca similar to that in the original spinel with some K. The potassium

FIGURE 40. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ anode 2416 after 131 hours with open circuit (see Figure 30 for corresponding cathode 1416).

FIGURE 41. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ anode 2417 after 24 hours with current density of 1.1 amps/cm^2 (see Figure 31 for corresponding cathode).

FIGURE 42. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ anode 2419 after 18 hours with current density of $\sim 0.9 \text{ amp/cm}^2$ (see Figure 38 for corresponding cathode 1419).

PLASMA SURFACE

MgO INSULATOR

FIGURE 43. Microstructure of $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ anode 2416 cross section (see Figure 40).

in this phase decreased, and at ~0.3 cm below the surface, only trace amounts were found in the second phase (Figure 43c).

On the back surface adjacent to the copper current leadout, there were localized areas with high concentration of K(18%) (Figure 43d). These areas were depleted in Fe(29%) and Mg(1%) but high in Al(16.9%). These areas of high K decrease as the distance from the anode back surface increases, 3.7% K at 0.04 cm and 0.1% K at 0.09 cm. The matrix surrounding these areas of high potassium were the original spinel composition.

Anode 2419. This anode (Figure 42) also showed similar microstructures and compositional changes to the 2416 anode except the recrystallized portion was more extensive and the Pt current leadout separated. The fracturing along the grain boundaries was also more severe.

3.3.3.4 $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$

The performance of two hercynite-magnetite electrodes fabricated by hot pressing at MIT and LASL was the same. The electrode surfaces exhibited extensive melting, flow, and/or erosion (Figures 44 and 45). The recession of the cathodes was more severe, being as much as 0.5 to 0.8 cm or up to 50% of the original sample height. The recession of the anode was less, ~0.1 to 0.2 cm, forming a concave depression with the center slightly downstream from the midpoint between the side insulators. The recession was progressively greater on the downstream anodes.

The anodes reacted with the MgO side insulation and in the cathodes. This was so extensive that it completely covered portions of the downstream electrodes, especially on the cathodes, e.g. cathode 1524 (Figure 44) was completely covered in the cross section examined. This cap was a mixture of iron spinel and MgO.

Portions of the electrodes which did not react with the MgO did exhibit microstructure change, forming basically two phases, one very high in Fe (60%), depleted in Al (23%), and high in K (16%). The other was localized areas of nearly pure iron oxide. The concentration of each of these phases varied within the electrodes. The top surfaces of the exposed anodes was depleted in iron.

FIGURE 44. Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1524 after 75 hours at 1.1 amps/cm^2 (see Figure 45 for corresponding anode 2514).

FIGURE 45 Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ anode 2524 after 75 hours at $\sim 1.1 \text{ amps/cm}^2$ (see Figure 44 for corresponding cathode 1514).

The potassium was concentrated in areas rich in aluminum or at the grain boundaries along with impurities such as silicon and calcium.

The degradation of the cathodes were substantially greater than that of the anodes.

- Reactions with MgO were less.
- Microstructural changes at top surface were less, but both represented a depletion in iron.
- Most of the anodes underwent little microstructural changes. The overall composition was essentially the same as the original hercynite-magnetite spinel but depleted slightly in iron.
- The seed was concentrated near the top of the anode in bands associated with the grain boundaries which were also high in aluminum and silicon and in a second phase high in aluminum.
- The formation of two phase regions in the anode was limited to the higher temperature portions of the anodes.

Two electrodes are described in detail as examples.

Cathode 1524. The top of this hercynite-magnetite cathode was completely covered with a cap, (~0.3 cm thick) formed by the reaction of the insulator and electrode (Figures 44 and 46). The cap contained a number of phases which varied widely in composition depending upon their proximity to the insulator and electrode. The large light colored area at the upper left of the figure is rich in iron, Fe (38.4%), Al(10.4%), Mg(10.4%), O(39.7%), with the surrounding areas containing a second phase high in magnesium but free of aluminum, Fe(16.3%), Al(0.6%), Mg(41.3%) and O(40.9%).

Other areas, near or at the surface of this cap were depleted in iron and high in aluminum, e.g., Fe(10.8%), Mg(12.9%), Al(24.1%), and O(51.4%) with the second phase containing magnesium, Fe(14.1%), Al(0.7%), Mg(46.5%), and O(49.5%) (Figure 47a). In all areas, the overall iron concentration was less than its original value.

PLASMA SURFACE

MgO INSULATOR

0.05 cm

FIGURE 46. Microstructure of $0.75\text{FeAl}_{204}\cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1524 cross section (see Figure 44).

At greater depths, further evidence of magnesium interaction, electrode decomposition, and iron loss were observed (Figure 47b). For example, ~0.3 cm from the top surface, the cap contains four phases: two major phases of equal volume Fe(21.4%), Al(19.4%), Mg(10.5%), O(48.2%) and Fe(32.5%), Al(14.0%), Mg(10.2%), O(41.9%). An impurity second phase was located at the grain boundaries Fe(11.5%), Zr(23.0%), Ca(11.0%), La(30.1%), Ce(6.4%), O(16.7%) and a moderate amount of a dark phase Fe(14.6%), Al(23.3%), Mg(11.8%), O(49.5%).

A multiphase acicular structure with matrix of Fe(19.2%), Al(26.2%), Mg(~1%), K(9.0%) and O(43.5%) and needles of Fe(44.4%), Mg(6.4%), Al(8.1%), K(1.7%) and O(39.0%), was found near the bottom of the cap adjacent to a relatively unreacted electrode (Figure 47c). This was the first indication of potassium.

The gap between the cap and the electrode had a high concentration of potassium. The portion of the electrode immediately below the crack which separated the cap from the base electrode also underwent intensive phase transformation (Figure 47d). The more solid, continuous phase was very high in iron and was aluminum depleted, Fe(62.3%), Al(5.4%), K(0.8%) and O(30.5%) with a needle-like phase throughout, Fe(14.9%), Al(23.1%), K(14.7%), and O(41.3%). The concentration of this second phase decreased as the distance from the top surface increased and below ~0.24 cm disappeared.

Near the bottom of the cathode, the structure changed only slightly, but was two-phase (Figure 48e). The matrix Fe(48.1%), Al(18.4%), and O(31.9%), which was near the original composition, contained a second phase very high in potassium and silicon at the pores and grain boundaries. The composition of this second phase was Fe(7.3%), Al(11.9%), Si(12.4%), K(22.4%), and O(45.1%).

At the bottom, the hercynite-magnetite again separated into a two-phase region (Figure 48f). Areas of nearly pure iron oxide Fe(74.1%), Al(1.3%), K(1.1%) and O(22.0%) were scattered throughout the matrix which was close to the original composition but slightly depleted in

FIGURE 47. Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1524; (a) near plasma surface, (b) 0.7 mm, (c) 3 mm, and (d) 5.5 mm from plasma surface (see Figure 46).

E

F

0.01 cm

FIGURE 48. Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ cathode 1524; (e) 6.2 mm and (f) 12 mm from plasma surface (see Figure 46).

iron, (Fe(43.7%), Al(18.9%), Mo(2.6%), K(2.3%) O(31.4%), and small amounts of other impurities.

Potassium seed concentration between the electrode and base insulator in the area of the current leadout was very high.

Anode 2524. The anode underwent substantially less degradation than the corresponding cathode (Figure 45). However, some similarities were observed in the microstructures of the anode and cathode. The top surface exposed to the plasma underwent microstructural changes, forming a loose, vesicular structure. Less than 0.1 cm of the surface restructured extensively, although there had been substantial erosion.

The dense particles, which separated from the surface, were depleted in iron with small amounts of magnesium [Fe(23.3%), Al(24.0%), and O(48.4%]. Breakup of the surface may be associated with the formation of an acicular, two-phase structure near the spinel surface. The matrix contained Fe(31.0%), Al(20.0%), Mg(2.6%) and O(45.4%), while the needle-like phase contained Fe(38.3%), Al(17.0%), Mg(2.3%), and O(41.3%), suggesting the incipient separation into high Fe and high Al phases. This latter phase also was found in the grain boundaries.

A dark second-phase was observed at the grain boundaries and pores in adjacent areas which recrystallized and were near the original composition. This phase was high in potassium, Fe(5.2%), Al(12.4%), Si(13.3%), K(21.3%), and O(47.8%).

The top half of the remaining anode, below the thin recrystallized surface, also exhibited significant microstructural change. This top half appears as two bands of varying thickness (0.1 to 0.25 cm) and of varying depths (0.2 to 0.5 cm from the top surface). The top band was a two-phase acicular structure with a near original composition, Fe(16.5%), Al(26.6%), K(6.0%), and O(50.3%) (Figure 49a). The concentration of this second-phase decreased as the distance from the top surface increased. Breakup of the electrode appeared to originate at the grain boundaries. The bottom band is similar to the original structure; however, the original light second phase at the grain boundaries has changed with a second phase

A

0.005 cm

B

0.1 mm

C

0.01 cm

D

FIGURE 49. Microstructure of $0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ anode 2524; (a) near plasma surface, (b) 2.5 mm, (c) 3.5 mm, and (d) 10 mm from plasma surface (see Figure 45).

depleted in Al(11.7%) and Fe(40.4%), with 46.1% O surrounded by a matrix of Al(17.7%), Fe(14.3%) and O(37.2%) with minor impurities (Figure 49b).

At ~0.6 cm from the top surface and ~0.5 cm from the bottom of the electrode, the composition and microstructure of the anode was similar to that of the original material. The original anode contained a large amount of a light-colored, iron oxide second phase at the spinel grain boundaries, Fe(71.4%), Al(1.0%), Mg(1.0%), and O(25.4%) (Figure 49c). This phase was observed in the bottom 0.6 cm of the anode in the top. In addition, there were darker minor second phases which were high at potassium, e.g. Fe(24.2%), Al(11.8%), Si(12.6%), and K(14.5%). These two second phases were found all the way to the current leadout interface (Figure 49d).

The sides of the anode exhibited substantial microstructural change at the surface, especially near the midpoint of the anode. These surface changes resulted in an irregular growth (~0.001 cm thick) of dense iron oxide Fe(69.7%), O(27.8%), Al and Mg(1.4%). A band, ~0.015 cm thick, of the original hercynite-magnetite compositions, was now a two-phase acicular structure, similar to that observed in other areas of the anode, except the concentration was greater and the reaction layer was very well defined.

3.3.3.5 La(Mg)CrO₃

The behavior of the $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ and $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ electrodes was very similar (Figures 50-53). Although there were differences in the microstructures after the test, these differences cannot be related solely to the starting microstructures or compositions.

The cathodes degraded significantly more than the anodes exhibiting greater fracture and reaction with seed. However, anode 2630 (Figure 53) appears to be an exception, experiencing more change than any other anode or cathode. The cathodes fractured into relatively large pieces, especially at the top corners. In most cathodes, a crack runs parallel to and ~0.4 cm below the surface. With the exception of anode 2630, the fracture of the anodes was minimal.

Although difficult to measure because of surface breakup, it appears that the electrodes eroded approximately 0.1 cm; however, the cathodes decreased 10 to 20% in width. Perhaps this is related to a reaction layer

FIGURE 50. Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ cathode 1627 after 615 hours at $\sim 1 \text{ amp/cm}^2$ (see Figure 51 for corresponding anode 2627).

FIGURE 51. Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ anode 2627 after 61.5 hours at 1.1 amps/cm^2 (see Figure 50 for corresponding cathode 1627).

FIGURE 52. Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ cathode 1630 after 75 hours at $\sim 0.2 \text{ amp/cm}^2$ (see Figure 53 for corresponding anode 2630).

FIGURE 53. Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ anode 2630 after 75 hours at $\sim 0.2 \text{ amp/cm}^2$ (see Figure 52 for corresponding cathode 1630)

on the sides and bottom of the cathodes. The thickness of this reacted layer varied up to 0.05 cm.

The top 0.2 to 0.3 cm of both anodes and cathodes were extensively changed, forming a laminated structure which was often separated by areas of high porosity. These areas of exfoliation were generally associated with the loss of chromium resulting, for example, in the formation of nearly pure lanthanum oxide on the surface. Impurities from upstream component insulators and electrodes contaminated the surfaces. The chromium concentration increased as the distance from the surface increased, and at the bottom of the exfoliation, the chromium content was the same as that of the original chromite.

Potassium in the electrodes was low and concentrated in the pores. Concentration of potassium in the cathodes was greatest in a band approximately 0.4 and 0.8 cm below the top surface. Seed also penetrated into the MgO insulators adjacent to the cathodes, especially those which had high current densities for long periods. Reaction of the chromite electrodes with the MgO insulators was minimal.

The microstructures representative of specific anodes and cathodes are described in more detail.

Cathode 1627. The cathode experienced substantial breakup and fracture especially at the top and bottom (Figures 50 and 54). Approximately 0.2 to 0.25 cm of the top separated from the bulk of the electrode. Only at the top near the high temperature plasma was there any indication of electrode insulator interaction. The copper current leadouts separated from both the $\text{La}(\text{MgCrO}_3)$ and the MgO. This area was an area for high seed concentration.

The top surfaces of the cathodes were extensively degraded and exfoliated. The larger high density particles partially separated from the top surface and vary in composition (Figure 55a). The topmost surface was mostly La(65.9%) with only 8.1% Cr (Figure 55b and 55c). However it contains many impurities--Fe(6.3%), Zr(5.5%), Ca(2.1%), Al(1.5%) and Mg(2.1%) which may be contaminants from other components of the channel and combustor. The minor second phase, which was found only in localized areas, was nearly pure MgO with only 1.2% La.

a

PLASMA SURFACE

b

c

0.05 cm

FIGURE 54. Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_2$ cathode 1627 showing lanthanum oxide formation and chromium loss from surface (see Figure 50).

0.01 cm

FIGURE 55. Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ cathode 1627 (see Figure 54).

The composition of these particles change, becoming more like the starting cathode composition but still depleted in Cr (Figure 56a and b). At the bottom of one large particle, ~0.3 cm across, the Cr was only 11.4% compared to ~19% for the original chromite.

The exfoliation of the cathode was approximately 0.2 cm thick. The top of this area was nearly all La(67.2%) with less than 1% Cr (Figure 56b and c). However, it did contain significant Si(7.7%), Ca(4.6%) and Ce(1.0%) plus other minor impurities. The first indication of K(0.3%) was observed in this area. The Cr content increased and La decreased as the distance from the surface increased (Figure 56a and b). At the bottom of the area of breakup, the La had decreased to 62.8% while the Cr had increased to 5.5%, but still about one-third the original concentration. The Si(5.8%), Ca(3.2%), Ce(0.7%) and K(0.2%) impurities remained. The remainder of the La(Mg)CrO_3 appeared to be essentially identical to the original cathode (Figure 56c).

A similar reaction layer also covered the sides and bottom, resulting in surface breakup (Figure 56c). The particles, which separated from the intact surface, were high in La(74.2%) and depleted in Cr(5.5%). However, the high concentration of Si, Ca and Ce were not present.

Many small oxide particles, now enclosed in resin, were found in the top portion of the cathode in the spaces between the cathode, the larger surface particles and the MgO. The particles were nearly pure lanthanum oxide and appeared to have broken off from the surface of the cathode.

Potassium was often found near pores and cracks in areas of exfoliation. These areas of high potassium were also areas depleted in lanthanum, e.g., Cr(18.3%), K(16.9%), La(20.7%), and O(41.5%). However, most potassium was concentrated in pores located in the top half of the cathode or above the large crack, ~0.4 cm below the surface.

Anode 2627. The La(Mg)CrO_3 had remained relatively intact, with only very minor cracking compared to the cathode (Figure 51). The Ca and Cu-Ag braze remained attached to the MgO but separated from the anode. There was very little reaction between the anodes and the side MgO insulators,

FIGURE 56. Microstructure of $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$ cathode 1627 (see Figure 54).

except at the top of the anode. The anode eroded very little, although degradation of the top had caused the surface to swell and break up. Between 1.3 to 1.4 cm of the original 1.6 cm thick anode remained.

The typical composition of the apparently unaffected areas below the exfoliated surface was identical with sibling reference samples. It was, however, difficult to detect the presence of magnesium. The measured composition was La(66.1%), Cr(19.0%), and O(14.1%) with between 0.1 and 0.2% impurities of Al, Si, K and Pd. This consisted of a matrix of 64.6% La, 19.9% Cr and 14.7% O. This second phase, $\sim 3 \times 10^{-4}$ cm across, was nearly pure La_2O_3 , with La(69.4%) and Cr(4.7%).

The degradation and ultimate breakup and expansion of the hot anode surface, like that of the cathode, apparently resulted from the loss of chromium and formation of lanthanum oxide. Very dense particles on the topmost surface were single phase lanthanum oxide and little chromium, with impurities of Al(3.7%), Fe(5.3%) and Zr(4.2%).

In the next lower layer, there was a two-phase, low density area with the matrix of La(77.5%) with 5.8% Si, while the darker second phase contained near the starting La/Cr composition, but was slightly La rich.

The next layer was also two-phase, with the matrix near the original La and Cr composition, while the second phase was chromium depleted with a high Si content (5.7%). Potassium (1.4%) was also found in this latter Si containing phase.

A sharp interface of reacted and unreacted chromite was found in the last layer. Immediately above this sharp demarcation, the electrode was two phase with a near starting composition, a few impurities and some potassium. The small amount of second phase again was chromium depleted (8.5% Cr) and also contained P(4.1%) and K($\sim 1\%$).

On the other side of the reaction line, the structure and composition were that of the reference electrode. This composition continued to the bottom of the electrode. Only small amounts of potassium were found in this region.

A thin reaction layer was formed on the electrode wall adjacent to the MgO insulator. It extended over most of the unreacted side portion of the electrode. This layer, 0.5 to 1.5×10^{-5} cm thick, was tightly bonded to the electrode. The layer was depleted in Cr(12.1%), with La(60.4%) and O(11.1%). The reaction boundary was very sharp with the unreacted material free of phosphorous and identical to the starting reference chromite composition and structure. The source of the phosphorous is not known but this layer was probably the source found near the reaction boundary at the top of the electrode.

3.3.4 Summary and Conclusions

The following conclusions from the characterization and evaluation of Phase II U-02 test are summarized.

3.3.4.1 MgO Insulators

- The MgO side insulators (90% TD) were more extensively fractured than the base insulators (85% TD). Fracture generally occurred near the bottom of the electrodes, with cracks running parallel to electrode surface. This is undoubtedly related to larger temperature gradients in the side insulators.
- The MgO reacted in varying degrees with all of the electrode materials--most intense near the plasma surface. Reaction was most severe with iron aluminum, magnetite spinel and magnesium aluminum-iron spinel. The least reaction was observed with the ZrO_2 - CeO_2 base electrodes. The reaction with the $La(Mg)CrO_3$ was minimal, but more than the ZrO_2 - CeO_2 electrodes.
- The top surfaces of the MgO exposed to the plasma had undergone extensive microstructural changes to depths between 0.2-0.4 cm.
- Potassium seed penetration was greatest in the cathode insulators than in the anode insulators, in those with highest current densities and longest times with current flow. Penetration is through pores and concentrates in MgO insulators adjacent to and below the electrode-current lead-out-base insulator interfaces.

3.3.4.2 Current Leadouts

- The Pt and Cu-Au current leadouts which originally bonded the electrode to the base electrode had separated in the majority of electrodes. Separation was in most cases from the electrodes or from both electrode and insulator. The Inconel current leadouts, especially for the cathodes, had reacted extensively with the MgO insulators.

3.3.4.3 Electrodes

- Many of the $\text{CeO}_2\text{-ZrO}_2$ base cathodes were lost during the test, exposing the MgO insulation to the plasma. Only portions of the anodes were lost. This loss can be attributed to a combination of factors.
 1. Separation of metal current lead-out from base of the electrode.
 2. Fracture of side insulators and resultant loss of retaining capacity.
 3. Unknown factors associated only with cathode, e.g. seed affects.
 4. The electrodes were relatively thin resulting in a high back surface temperature.
- The iron-aluminum and iron-magnesium-aluminum spinels and the La(Mg)CrO_3 electrodes all remained intact although the side insulators were fractured and some current lead-outs separated. The thickness of the electrodes may have been a factor because of better mechanical attachment and lower back surface temperature.
- The apparent melting of the hercynite-magnetite electrodes resulted in gross downstream surface contamination of the La(Mg)CrO_3 electrodes.

$\text{CeO}_2\text{-ZrO}_2\text{-Ta}_2\text{O}_5$ Graded Electrodes

- The electrodes which remain had fractured ~ 0.2 cm from bottom with the cracks running the entire width of the electrode parallel to the surface. This corresponds to the boundary between the $0.75 \text{ CeO}_2\text{-}0.25\text{ZrO}_2$ and $0.78\text{CeO}_2\text{-}0.20\text{ZrO}_2\text{-}0.02\text{Ta}_2\text{O}_5$ compositions. Some evidence of smaller cracking was observed in the pretest electrodes.
- The microstructures of both anodes and cathodes has been modified with extensive microstructural changes on top (up to 0.25 cm) of the electrode.

- All electrodes appeared to be single phase and contained only minor amounts of potassium. This extensive restructuring is apparently related to the separation of electrodes from base insulator and resultant heat barrier causing possible higher overall electrode temperatures.

- The entire microstructure was modified similar to the graded electrodes.
- The sides of the electrode have undergone extensive erosion due to side insulator loss resulting in exposure of the cathode.
- The cathode had operated for some time separated from the base insulator as evidenced by build-up of porous $\text{MgO} \cdot \text{CeO}_2 \cdot \text{ZrO}_2$ material between the cathode and insulator.

- Performance of cathode samples prepared by two fabricators (BNW and Transtech) was the same.
- Cathodes exhibited extensive erosion at plasma surface with recession of the surface resulting in approximately 25% loss of electrode (1.3 cm to 0.9 to 1.0 cm). One cathode (1419) eroded 66%.
- All electrodes reacted with the adjacent MgO insulator to depth of as much as 0.56 cm from recessed surfaces.
- The top portion of the cathodes recrystallized to depth of up to 0.5 cm, with some evidence of melting and plastic flow at surface. The microstructural changes were greater for those which operated at the higher current densities and for the longest times.
- The portion of the electrode which had not restructured has in most instances exhibited extensive fracture along the grain boundaries.
- The top, 0.01 to 0.02 cm, surfaces of the electrodes is an iron depleted layer of either MgAl_2O_4 or high MgO- MgAl_2O_4 (downstream) which also contains a significant second phase of calcia stabilized zirconia. This combination is probably the whitish surface observed on the electrode at the termination of the test.

- The restructured portion of the $0.75\text{MgAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$ underwent extensive multiphase compositional changes. The make up and distribution of these phases is complex, with up to three different phases in some portions of the recrystallized area. In general, there has been a compositional change into Fe rich and iron depleted phases which contain different amounts of aluminum and magnesium. For example, immediately below the iron depleted top layer is a three phase region with a matrix of $\sim 18\%$ Fe, 1% Al, 45% Mg, and 38.5% O^* . The other major phase is 6% Fe, 32% Al, 12% Mg, and 49% O. The amount and compositions of these phases change as the distance from the surface increases. There are localized areas of nearly pure iron oxide.
- Seed is localized in the areas of high aluminum and in grain boundary areas which originally contained high Ca and Si.
- The anode also underwent microstructural and compositional changes; however, they are not as extensive as the cathode, nor are the compositions the same.

$0.75\text{FeAl}_2\text{O}_4 \cdot 0.25\text{Fe}_3\text{O}_4$

- Performance of the hercynite-magnetite electrodes fabricated by the two different sources (MIT and LASL) was the same.
- The electrodes surfaces exhibited extensive melting and flow. The flow downstream was extensive and contaminated downstream electrodes.
- The electrodes reacted with the MgO insulators, and in the cathodes this was so extensive that it completely covered some electrodes. This cap was a mixture of iron spinel and MgO.
- The portion of the cathode unreacted with MgO underwent extensive microstructural changes, forming basically two phases; one very high in iron (62% Fe, 5% Al) and the other depleted in iron (15%) and enriched in aluminum (23%) with high potassium (16%). There were some localized areas of nearly pure iron oxide.
- Potassium seed is concentrated in the areas rich in aluminum or in the grain boundaries along with impurities such as Si.

*Weight percent

- The degradation of the anodes was substantially less than cathodes.
 1. Reaction with MgO was less.
 2. Microstructural changes at top surface were less, but represented a depletion in iron.
 3. Most of the anodes underwent little microstructural changes. The overall composition was essentially the same as the original hercynite-magnetite spinel but depleted slightly in iron.
 4. The seed is concentrated near the top of the anode in bands associated with the grain boundaries which are also high in aluminum and silicon and in a second phase high in aluminum.
 5. The formation of two phase regions in the anode was limited to the higher temperature portions of the anode.

La(Mg)CrO₃

- The behavior of the La_{0.95}Mg_{0.05}CrO₃ and LaMg_{0.05}Cr_{0.95}O₃ were approximately the same.
- The cathode had degraded significantly more than the anode.
- The cathodes fractured especially at the top corner and bottom. In most cathodes, a crack runs parallel to and ~0.4 cm below the surface.
- The top 0.2 to 0.3 cm of both anode and cathodes underwent extensive change, forming a laminated structure, often separated by areas of high porosity.
- The surface layer exposed to the plasma is nearly pure lanthanum oxide with impurities from upstream components.
- The chromium concentration increases as the distance from the surface increases.
- The exfoliation of the surface is attributed to the vaporization loss of chromium and formation of La₂O₃.
- Potassium in electrodes is low and is concentrated in pores. Concentration is greatest between 0.4 and 0.8 cm below top surface.

3.4 Characterization-Evaluation of MHD Materials

3.4.1 Thermal Diffusivity/Conductivity

3.4.1.1 Arc Plasma Sprayed Electrodes and Insulators. Arc plasma spraying of electrode and insulator materials is being seriously considered as a method for fabricating electrode/insulator/current leadout for channel MHD systems. However, the material deposited during arc plasma spraying may have properties and structures substantially different from that of the higher density materials fabricated by sintering or hot pressing. This process generally results in lower densities and often with inhomogeneous, stressed and thermally unstable structures. Previous thermal diffusivity/conductivity and thermal expansion measurements⁽⁹⁾ show the arc plasma sprayed oxides, i.e. Al_2O_3 , HfO_2 , Y_2O_3 and CaO stabilized ZrO_2 to have thermal conductivities up to four times lower than for the same oxide prepared by sintering or hot pressing. In addition, both the thermal diffusivity/conductivity and thermal expansion change significantly as the oxides are heat treated. Therefore, it is important that these thermal and structural properties be determined for the arc plasma sprayed electrode and insulator materials.

$\text{La}(\text{Mg})\text{CrO}_3$. The thermal diffusivity of an arc plasma sprayed $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ was measured to $\sim 1900^\circ\text{K}$ during three heating cycles. The geometric density of the sample was $\sim 5.84 \text{ g/cm}^3$, $\sim 88\%$ TD. After measurement, there was only insignificant change ($<1\%$) in sample thickness; however, the 0.625 cm diameter sample, 0.060 cm thick, bowed $\sim 0.003 \text{ cm}$.

The measurements were made in argon at one atmosphere. The thermal diffusivity increased as the measurement temperature increased (Figure 57). After the first heating cycle to 1183K, only a slight permanent increase was observed in subsequent diffusivity measurements below 1180K. The second heating cycle to 1638K resulted in another slight permanent increase in thermal diffusivity. However, heating between $\sim 1650\text{K}$ and 1905K resulted in a significant permanent increase in the thermal diffusivity. Heating at $\sim 1900\text{K}$

FIGURE 57. Thermal Diffusivity of plasma sprayed La_{0.95}Mg_{0.05}CrO₃.

for one hour did not result in any further diffusivity increase. On cooling, the thermal diffusivity was 1.5 times greater than that of the as-sprayed chromite. The final thermal diffusivity values are about 6-7% lower than that for hot pressed La(Mg)CrO_3 (Figure 57).

The data on cooling after heating to 1905K also show some irregularities in the α versus T curve between 1525-1725K. Similar effects were observed for the hot pressed chromite between 1500 and 1700°C. These results suggest possible phase changes in the La(Mg)CrO_3 in this temperature range. Loss of chromium may also have occurred as evidenced by the pink coloration of the Al_2O_3 sample holder in the areas contacted by the La(Mg)CrO_3 .

Further thermal diffusivity studies of other arc plasma sprayed electrode and insulator materials will be conducted. These studies must be correlated with evaluations of the microstructures and thermal expansion data. The latter measurements will be made when larger arc plasma sprayed samples can be prepared.

$0.82\text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.10\text{Y}_2\text{O}_3$. The thermal diffusivity of hot pressed $0.82\text{HfO}_2 \cdot 0.18\text{CeO}_2 \cdot 0.10\text{Y}_2\text{O}_3^+$ was measured to 1988K in argon (Figure 58). The room temperature density of the hot pressed sample was multiphase with approximately 75% monoclinic HfO_2 , 25% f.c.c. Y_2O_3 stabilized HfO_2 and 2% f.c.c. CeO_2 , with a combined density of 8.16 g/cm^3 (see Section 3.1.2.2). The thermal conductivity was calculated from heat capacity data, room temperature density corrected for measured thermal expansion data and measured thermal diffusivity (Figure 59). The measured thermal expansion measured in air fits two straight lines

$$\alpha_{(325-925\text{K})} = 6.82 \times 10^{-6}/\text{K}$$

$$\alpha_{(925-1725\text{K})} = 8.17 \times 10^{-6}/\text{K}$$

The coefficient of determination was >0.99 . The heat capacity for this multiphase mixture was calculated from measurement data⁽¹⁰⁾ for HfO_2 , Y_2O_3 and CaO_2 using a theory of mixtures.

⁺Sample prepared at Argonne National Laboratory.

FIGURE 58. Thermal diffusivity of hot pressed $0.82\text{HfO}_2 \cdot 0.08\text{CeO}_2 \cdot 0.10\text{Y}_2\text{O}_3$.

FIGURE 59. Thermal conductivity of hot pressed 0.82HfO₂·0.08CeO₂·0.10Y₂O₃.

The thermal conductivity exhibits significant changes on heating, with an increase near 1400K and a decrease near 1700K. A hysteresis is observed on cooling which also shows an irregularity near 1700K. Below ~725K, the data on heating and cooling are approximately the same. These irregularities in α versus T curves and the hysteresis on heating and cooling probably reflect possible phase changes in this multiphase sample.

4.0 WORK ANTICIPATED DURING NEXT QUARTER

4.1 Electrochemical Effects

The testing and evaluation of seed/slag in a dc electric field on MHD electrodes and insulators will continue. The preliminary testing of lanthanum chromites will be completed. Testing of other electrode materials such as hafnium oxide and some insulator materials in molten potassium sulfate electrolyte will be made. Testing in molten coal slag will also be emphasized.

4.2 Electrode-Insulator Development

The hot pressing evaluation of graded electrodes by Eagle Picher will be completed. A study for fabricating insulator materials, e.g., MgAl_2O_4 with low density (for thermal shock resistance) and total closed porosity will be initiated using techniques similar to those for fabricating magnesium aluminum-magnesite spinel.

4.3 Characterization and Evaluation

The characterization of potential materials for the U-02 Phase III test will be started. Special emphasis will be placed on the properties and structure of arc plasma sprayed materials.

REFERENCES

1. Joint U.S.-U.S.S.R. Test of U.S. MHD Electrode System in U.S.S.R. U-02 MHD Facility - Phase I. ERDA-76/154. W. E. Hosler, Ed. National Bureau of Standards (1976).
2. J. Lambert Bates, Development, Characterization and Evaluation for Open Cycle MHD. Quarterly Report for Period Ending December 19, 1976. BNWL-2004-5 (1977).
3. Joint Report on the Joint U.S.-U.S.S.R. Test of the U.S. Electrode System in the U-02 Facility - Phase III. Westinghouse Research and Development Laboratories, Pittsburgh, PA. To be published (1977).
4. S. J. Schneider, et al, "Joint Test of a U.S. Electrode System in the U.S.S.R., U-02 Facility," Proceedings of the 15th Symposium, Engineering Aspects of Magnetohydrodynamics, Philadelphia, PA., May 24-26 (1976).
5. J. Lambert Bates, Properties of Molten Coal Slags Relating to Open Cycle MHD, BNWL-B-466, December 1975.
6. G. Rudins, S. J. Schneider, T. Negas, B. R. Rossing, J. L. Bates, G. P. Telegin, T. I. Borodina, Ya. L. Dolinsky and V. I. Zaekind, The Second Joint Test of a U.S. Electrode in the U.S.S.R. U-02 Facility, 16th Symposium, Engineering Aspects of Magneto Hydrodynamics, University of Pittsburgh, May 16-18, 1977, pp IV.1.1-12.
7. Private Communication, T. Negas, National Bureau of Standards, Gaithersburg, MD.
8. H. P. R. Frederikse, T. Negas and S. J. Schneider, Development, Testing and Evaluation of MHD Materials, Quarterly Report, October-December 1976, Dec. 1976, E(49-1)-3800-6.
9. K. E. Wilkes and J. F. Lagedrost, Thermophysical Properties of Plasma Sprayed Coatings, NASA CR-121144, March 1973.
10. Y. S. Touloukian, R. W. Powell, C. Y. Ho and Nicolaou, Thermophysical Properties of Matter, Vol. 5, Plenum Press, New York (1973).

DISTRIBUTION

OFFSITE

No. of
Copies

No. of
Copies

A. A. Churm ERDA Chicago Patent Group 9800 South Cass Ave. Argonne, Illinois 60439	H. Kent Bowen Massachusetts Institute of Technology 77 Massachusetts Avenue Cambridge, Massachusetts 92139
5 Joe Morris ERDA Division of MHD 20 Mass. Ave Washington, DC 20001	Thomas R. Brogan MEPPSCO, Inc. 141 Pearl Street Boston, Massachusetts 92110
2 G. Rudins ERDA Division of MHD 20 Mass. Ave. Washington, DC 20001	Vernon Griffiths Montana Colledge of Mineral Science and Technology West Park Street Butte, Montana 59701
M. Raring ERDA Division of MHD 20 Mass. Ave. Washington, DC 20001	2 Jerry D. Plunkett/J. J. Rasmussen Montana Energy and MHD Research Institute Butte, Montana 59701
2 M. Petrick/K. Kuczyn Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439	Dennis Blackketter Montana State University Bozeman, Montana
S. W. Petty Avco Everett Research Laboratory 2385 Revere Beach Parkway Everett, Massachusetts 02149	4 Samuel J. Schneider/H. Frederiske Materials Building National Bureau of Standards Washington, DC 20234
Vance Cooper Electric Power Research Institute P.O. Box 10412 Palo Alto, California 94303	Daniel Bienstock/R. J. Wright Pittsburgh Research Center Energy Research and Development Adm. 4800 Forbes Avenue Pittsburgh, Pennsylvania 15213
David G. DeCoursin Fluidyne Engineering Corporation 5900 Olson Memorial Highway Minneapolis, Minnesota 55422	Robert H. Eustis Mechanical Engineering Department Stanford University Stanford, California 94305

No. of
Copies

Sterge T. Demetriades
STD Research Corporation
P.O. Box C
Arcadia, California 91006

John B. Dicks/Russ Crawford
Energy Conversion Division
University of Tennessee Space Inst.
Tullahoma, Tennessee 37388

- 2 Barry R. Rossing
Westinghouse Research Laboratories
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

328 ERDA Technical Information Center

- 3 ERDA Richland Operations Office
F. L. Goldsberry
Programs Office
H. E. Ranson

41 Battelle-Northwest

(20)
J. L. Bates
L. R. Bunnell
T. D. Chikalla (2)
J. L. Daniel
J. W. Finnigan
J. C. Fox
P. E. Hart
D. D. Marchant
R. P. Marshall
G. B. Mellinger
R. E. Nightingale
D. E. Olesen
L. C. Schmid/J. Cox
G. L. Tingey
P. C. Walkup
Technical Files(5)
Technical Publications