Development and Characterization of Materials for Open Cycle MHD

Quarterly Report for the Period
April - June 1976

by
J. Lambert Bates
Principal Investigator

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	ii
ABSTRACT	iii
1. OBJECTIVE	1
2. SCOPE	1
3. TECHNICAL PROGRESS	2
3.1.1.1 Thermal Conductivity Calculation Methods	2
3.1.1.2 Specific Heat Calculations	4
3.1.1.3 Thermal Conductivity Results	5
4. DEVELOPMENT OF MATERIALS	4
4.1 Fabrication of Electrode Materials	12
4.2 Metal Current Leadout	19
4.2.1 Fusion of Metal Current Leadout	19
4.2.2 Sputtered Coating	19
5. WORK ANTICIPATED DURING NEXT QUARTER	20
5.1 Characterization of Materials for US-USSR U-02 Phase II MHD Channel Test	20
5.2 Electrode and Insulator Fabrication	20
6. FABRICATION OF ELECTRODES	20
REFERENCES	22
DISTRIBUTION	23

List of Figures

1. Thermal Conductivity of Phase I ZrO_2 Base Electrode Materials
2. Thermal Resistivity of $0.5 \text{ CeO}_2 \cdot 0.5 \text{ ZrO}_2$ Electrode
3. Thermal Resistivities of ZrO_2 Base Electrode Materials
4. Thermal Conductivity Variation at 1000°K as a Function of Open Porosity
5. Microstructural Cross Section of Some Electrode Oxides Used to Measure the Thermal Diffusivity. (As Polished)
6. Microstructures of $0.75 \text{ Mg Al}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ with Controlled Porosity. See also Figure 7.
7. Microstructures of $0.75 \text{ Mg Al}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ with Controlled Porosity. See also Figure 6.
8. Microstructures of $0.75 \text{ Mg Al}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$ Showing Sharp Gradations of Porosity
9. Sputtered Nickel Coating on Dense (a) and Porous $3 \text{ Mg Al}_2\text{O}_4 \cdot \text{Fe}_3\text{O}_4$. The Ni coating is approximately 0.0002-0.0003 cm Thick.

CHARACTERIZATION, DEVELOPMENT AND EVALUATION
OF MATERIALS FOR OPEN CYCLE MHD

J. Lambert Bates (Principal Investigator)

L. R. Bunnell
J. L. Daniel
P. E. Hart
G. B. Mellinger

ABSTRACT

Characterization and development of electrode and insulator materials are being performed in support of the US-USSR MHD Power Generation Program. The characterization and evaluation of the materials from the Phase I, U-02 test has been completed and the development and fabrication for the Phase II test initiated. The procedures for fabricating $3 \text{ Mg Al}_2\text{O}_3 \cdot \text{Fe}_3\text{O}_4$ electrodes with controlled microstructures were developed. Electrodes for the Phase II test in the USSR U-02 are being fabricated. The study of methods for fabricating electrodes with controlled microstructures and graded compositions, and for applying metal current leadouts to high temperature MHD electrodes is continuing.

CHARACTERIZATION, DEVELOPMENT AND EVALUATION OF MATERIALS FOR THE US-USSR MHD PROGRAM

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1.0 OBJECTIVE

The objectives of this program are to provide technical and scientific support to the United States open cycle MHD program in materials characterization, development and evaluation.

2.0 SCOPE

The scope of this program encompasses four areas:

- Provide technical and scientific assistance to MHD Division of ERDA and participating contractors with respect to selection, fabrication, and characterization of materials for testing in USSR U-02 MHD generator.
- Assist in the planning, coordination, and monitoring of screening and channel tests and materials characterization relating to USSR U-02 materials testing.
- Characterize and evaluate the behavior of materials before and after testing in the U-02 MHD generator and in other related screening tests. The characterization includes chemical, structural, and thermophysical property measurements.
- Develop high temperature electrodes and insulator materials with controlled microstructures and compositions and ceramic to metal current leadout.

3.0 TECHNICAL PROGRESS

3.1 U-02 PHASE I MATERIALS

3.1.1 Thermal Conductivity

3.1.1.1 Thermal Conductivity Calculation Methods

The thermal diffusivities of the pretest electrodes and MgO insulator tested in the USSR U-02 (Phase I) were measured previously and have been reported.^(1,2) However, the thermal conductivity may be the property of most immediate interest to electrode and insulator design and performance. For this reason, the thermal conductivity (λ) was calculated from the thermal diffusivity (α), room temperature density (ρ), thermal expansion ($\Delta L/L$) and specific heat (C_p) by the equation

$$\lambda = \alpha \cdot \rho \cdot C_p \quad (1)$$

All of the above properties have been measured with the exception of the specific heat. The density at temperature (ρ) was calculated using the measured room temperature density (ρ_0) and the measured thermal expansion values using the equation

$$\rho = \rho_0 (1 + 3 \Delta L/L)^{-1} \quad (2)$$

The specific heat values were obtained from: (1) reported literature C_p data; (2) calculated values using the Kopp-Neuman Law where the molar C_p of a compound or alloy is equal to the sum of the product of the atomic specific heats of its constituent elements, i.e.

$$C_p = \sum_{i=1}^n X_i (C_p)_i \quad (3)$$

and/or (3) calculations using Debye's expression for C_p at high temperatures. In the latter calculations, the heat capacity at constant volume, C_v , approaches $3R$ above the Debye temperature, Θ , or

$$C_v = 5.95 \times (\text{number of atoms/molecule}) \quad (4)$$

However, to calculate the heat capacity at constant pressure, (C_p)

$$C_p = C_v + a^2 VT \beta^{-1} \quad (5)$$

where a is the volumetric coefficient of expansion; V is the molar volume

and β is the compressibility. The compressibility is inversely proportional to the bulk modulus (B) and elastic modulus (E)

$$B = \frac{E}{3(1 - 0.2\mu)} \quad (6)$$

where μ is Poisson's ratio and varies between 0.26 and 0.32. Thus, specific heat can be estimated if E is known as a function of temperature.

The volumetric thermal expansion can be calculated from the measured values of the linear thermal expansion, α

$$a = \left(\frac{\partial V}{\partial T} \right)_p V^{-1} = 3 \left(\frac{\partial V}{\partial T} \right)_p L^{-1} = 3\alpha \quad (7)$$

Therefore, the biggest unknown in calculating the thermal conductivity from the thermal diffusivity data for the Phase I U-02 materials appears to be the determination of the specific heat.

In most instances, e.g. for $\text{CeO}_2 \cdot \text{ZrO}_2$ and $\text{Y}_2\text{O}_3 \cdot \text{ZrO}_2$ there are sufficient data at lower temperatures, $\Theta/T < 1$, to apply the mixture method. However, at the higher temperature, which is of major interest on MHD electrodes, the data are limited or show a wider scatter in reported values.⁽⁴⁾ Therefore, it is helpful to use the Debye method to calculate the specific heats. This method can be used separately at high temperature where no values are available, or it can conveniently be used in conjunction with available lower temperature data and/or the theory of molar mixtures to obtain reasonable specific heat values over the entire temperature range.

The methods of molar volume mixtures was evaluated by calculating specific heats for some mixed oxides where reliable C_p data are available in the literature. For example, using molar mixtures, the calculated specific heat for CaO stabilized ZrO_2 at 1500°C is 0.185 cal/g-°C which falls in the center of the range of reported literature values, 0.17 to 0.20 cal/g-°C.

Calculations using the Debye method were made for ZrO_2 , CeO_2 and $\alpha\text{-Al}_2\text{O}_3$ and compared with reported values. Using 4.2×10^9 g/cm² (6×10 psi) for E and 0.26 for μ , the calculated C_p for ZrO_2 at 1500°C was 0.189 cal/g-°C compared to a reference value of 0.185 cal/g-°C. For $\alpha\text{-Al}_2\text{O}_3$ using 1.40×10^9 g/cm² (2×10^7 psi) for E and $\mu = 0.26$, the calculated C_p at

1500°C was 0.33 cal/g-°C compared to a recommended value of 0.31 cal/g-°C⁽⁴⁾ with some measured values as high as 0.35 cal/g-°C.⁽²⁾ For CeO₂, calculated values at 1500°C were 0.116 cal/g-°C compared to the measured 0.118 cal/g-°C. Thus, it appears possible to estimate C_p values to within ±5% using these methods.

3.1.1.2 Specific Heat Calculations

The specific heat values for MgO are known and recommended values over the entire temperature range of interest are available.⁽⁴⁾ Calculated MgO thermal conductivity values using the thermal diffusivity data have been reported previously.⁽¹⁾ These values are accurate to within ±5%.

However, for the zirconium base electrodes, materials containing Y₂O₃ and CeO₂, the specific heat data are lacking. Data for ZrO₂ (monoclinic) and CaO stabilized zirconia are reported; however, the data above 1000°C varies significantly. Limited but apparently valid data are available for Y₂O₃ and CeO₂. It therefore was possible to calculate the specific heats from 500 to 1600°C for the CeO₂-ZrO₂ and Y₂O₃-ZrO₂ electrode materials assuming a molar ratio average of the C_p for the three oxides. At higher temperatures, $\Theta/T > 1$, the values were verified by the Debye calculations, especially for ZrO₂. The specific heat of Y₂O₃ has been measured to 1000°C⁽⁴⁾ and this single set of values are used for these calculations.

The specific heat for CeO₂ has been measured by five investigators to 2000°C.⁽⁴⁾ The data agree up to 800°K, then the variations gradually increase as the temperature increases. The variation at 1000 and 1500°C is ~5% and ~10% respectively. The average values of the data were used.

The specific heat data for ZrO₂ shows little scatter to 1000°K.⁽⁴⁾ However, at higher temperatures the data varies substantially. Therefore, the measured values were used to 1000°C, and the Debye relationship was used to calculate C_p at higher temperatures, using reported values for the elastic modulus. The values agree with the measured values near 1000°K and fall within the band of reported values above 1000°K.

3.1.1.3 Thermal Conductivity Results

The thermal conductivities of the Phase I, U-02 electrode materials calculated from the thermal diffusivity data are tabulated in Table I and summarized in Figure 1. The calculated thermal conductivity of the $0.12 \text{ Y}_2\text{O}_3 \cdot 0.88 \text{ ZrO}_2$ can be compared with very limited data for an isostatic pressed and air sintered oxide to 86.7% TD.⁽⁴⁾ The conductivity from 200 to 1090°C increases very slightly with temperature from 0.0152 to 0.0165 watts/cm-°C respectively, (corrected to theoretical density). This is approximately 1 to 15% higher than the data in this study and shows a different temperature dependence. Considering the possible wide differences in structure resulting from fabrication, the agreement is very good. Data for comparison is not available for the $\text{CeO}_2\text{-ZrO}_2$ materials.

The thermal conductivities of the $\text{CeO}_2\text{-ZrO}_2$ electrode materials exhibit wide differences between samples. The shape of the λ versus T curves are similar below 925°C. However, above 925°C no consistent temperature variations in λ with composition can be observed, with some increasing and some decreasing. The cause of these variations could not be determined, although it could possibly be related to potential changes in stoichiometry since measurements were made in pure argon in a tungsten furnace where the oxygen pressures are low. The electrodes were sintered in air.

The differences in λ at all temperatures between the $\text{CeO}_2\text{-ZrO}_2$ electrodes far exceed the variations in the unknown values of the specific heats. This is evident from the calculated values for the $0.5 \text{ CeO}_2 \cdot 0.5 \text{ ZrO}_2$ electrode using the extremes in the calculated ZrO_2 specific heat data as illustrated in Figure 1 and Table 1. The thermal conductivities of these $\text{CeO}_2\text{-ZrO}_2$ electrodes should be very similar with some changes due to composition. These differences are probably related to microstructural differences and not compositional effects.

The unusual shapes of the λ^{-1} versus T curves also preclude the generation of the usual simple linear expression for λ^{-1} except that for the $0.5 \text{ CeO}_2 \cdot 0.5 \text{ ZrO}_2$ electrode, Figures 2 and 3.

$$\lambda^{-1} = A + BT \quad (8)$$

TABLE I. Calculated Thermal Conductivity Watts/cm°C

	0.12 Y ₂ O ₃	0.18 CeO ₂	0.50 CeO ₂ ⁽¹⁾	0.50 CeO ₂ ⁽¹⁾	0.75 CeO ₂	0.78 CeO ₂
	0.88 ZrO ₂	0.82 ZrO ₂	0.50 ZrO ₂	0.50 ZrO ₂	0.25 ZrO ₂	0.29 ZrO ₂
						0.02 Ta ₂ O ₃
Temperature °K	(Y-13)	(C-2-15)	I (C-3-22)	II (C-3-22)	(C-4-19)	(C-5-9)
400	0.0124					
500	0.0127					
600	0.0127					
700	0.0125					
800	0.0123	0.0151	0.0118	0.0117	0.0158	0.0187
850						
900	0.0120	0.0148	0.0115	0.0114	0.0152	0.0183
1000	0.0119	0.0143	0.0113	0.0111	0.0147	0.0177
1050						0.0175
1100	0.0119	0.0140	0.0112	0.0109	0.0144	0.0174
1150					0.0144	0.0172
1200	0.0120	0.0138	0.0110	0.0106	0.0144	0.0168
1250					0.0140	0.0161
1300	0.0121	0.0137	0.0109	0.0103	0.0133	0.0154
1350	0.0124	0.0137			0.0126	
1400	0.0127	0.0137	0.0105	0.0100	0.0121	0.0148
1450	0.0129	0.0138			0.0116	
1500	0.0129	0.0139	0.0101	0.00951	0.0111	0.0142
1550	0.0129	0.0141				
1600	0.0127	0.0145	0.00964	0.00899	0.0103	0.0137
1650	0.0126	0.0147				
1700	0.0127	0.0152	0.00932	0.00862	0.00973	0.0131
1750	0.0129	0.0159				
1800	0.0132	0.0162	0.00912	0.00837	0.00953	
1850		0.0174				
1900	0.0139	0.0187	0.00879	0.00801	0.00950	

(1) The thermal conductivities were for calculated using two different values for C_p which vary at high temperatures. The values for I are considered most reliable.

THERMAL CONDUCTIVITY 11-02 MHD ELECTRODES

Figure 1. Thermal Conductivity of Phase I ZrO₂ Base Electrode Materials

However, the data for $0.5 \text{ CeO}_2 \cdot 0.5 \text{ ZrO}_2$ can be separated into two linear portions, with the break at 1370°K . The linear equations are

$$\lambda = (66.52 + 0.02151 T)^{-1} \text{ watts/cm-}^\circ\text{C} [500 - 1370^\circ\text{K}] \quad (9)$$

and

$$\lambda = (34.29 + 0.04769 T)^{-1} \text{ watts/cm-}^\circ\text{C} [1370 - 1900^\circ\text{K}] \quad (10)$$

Although the curve shapes for the other electrodes are complicated above 1200°K , the slope of the λ^{-1} versus T curves below 1200°K are similar with slopes $\sim 0.154 \text{ cm/watt}$, with major differences being the constant A of equation (8).

From theoretical considerations, the constant B of equation (8) is a constant representative of intrinsic type properties, such as lattice parameter and composition. The constant A , in contrast, is more representative of extrinsic properties such as microstructure, etc. The similarity in constant B for all the $\text{CeO}_2\text{-ZrO}_2$ compositions and wider variations in A suggest that the differences in λ between these electrode materials is most probably not related to compositional differences, but to microstructural or related extrinsic properties such as porosity.

The thermal conductivity values appear to be directly related to the degree of open porosity. The thermal conductivities at 1000°K for the ZrO_2 base electrodes increase nearly linearly with the decrease in open porosity, Table 2 and Figure 4. [A similar increase is observed for a decrease in total porosity, although the scatter in the data is much greater.] These decreases in thermal conductivity with increases in porosity are substantially greater than that directly related to the variations in density. This suggests that the open porosity create thermal barriers which impede the transfer of heat.

TABLE 2. Density and Porosity of MHD Phase I Electrodes

	Density + g/cm ³		Porosity (%)	
	<u>TD</u>	<u>Measured (RT)</u>	<u>Open</u>	<u>Closed</u>
0.12 $\text{Y}_2\text{O}_3 \cdot 0.88 \text{ ZrO}_2$	5.80	4.855	17.7	<0.5
0.18 $\text{CeO}_2 \cdot 0.82 \text{ ZrO}_2$	6.29	5.164	15.8	2.1
0.50 $\text{CeO}_2 \cdot 0.50 \text{ ZrO}_2$	6.69	4.990	19.9	5.5
0.75 $\text{CeO}_2 \cdot 0.25 \text{ ZrO}_2$	6.96	5.505	17.6	3.3
0.80 $\text{CeO}_2 \cdot 0.18 \text{ ZrO}_2 \cdot 0.02 \text{ Ta}_2\text{O}_5$	7.04	5.935	14.6	1.1

THERMAL RESISTIVITY OF 50% CeO₂ · 50% ZrO₂ MHD ELECTRODE

Figure 2. Thermal Resistivity of 0.5 CeO₂ · 0.5 ZrO₂ Electrode

THERMAL RESISTIVITY OF ZrO_2 BASE MHD ELECTRODES

Figure 3. Thermal Resistivities of ZrO_2 Base Electrode Materials

THERMAL CONDUCTIVITY AT 1000°C VERSUS OPEN POROSITY

Figure 4. Thermal Conductivity Variation at 1000°K as a Function of Open Porosity

A close examination of the microstructures of the thermal diffusivity electrode samples show that the large, relatively dense particles are surrounded by a network of lower porosity made up of partially bonded, fine particles of oxide fines, Figure 5. These create large surfaces of unbonded oxide which can be considered as open pores. These obvious large surfaces act as discontinuities which impede the heat flow and substantially increase the thermal resistance. The heat must conduct across gaps or contacts which have significantly lower conductance than the oxide itself. Therefore, the greater number of these barriers which result from the open porosity, the lower the effective thermal conductivity. The marked difference between the microstructures of the $0.80 \text{ CeO}_2 \cdot 0.18 \text{ ZrO}_2 \cdot 0.02 \text{ Ta}_2\text{O}_3$ (C-5-9)(Figure 5d) compared with the $0.18 \text{ CeO}_2 \cdot 0.82 \text{ ZrO}_2$ (C-2-15)(Figure 5a) emphasizes the effect that difference in microstructure can make in the thermal conductivity values. Thus, if it is desirable to increase the thermal conductivity, the open porosity should be substantially reduced.

4.0 DEVELOPMENT OF MATERIALS

4.1 Fabrication of Electrode Materials

A major problem of refractory oxides as electrode materials for MHD is the general poor resistance to thermal shock. To reduce the susceptibility to this thermal mechanical failure, the oxides are generally fabricated with structures with lower porosity, with built-in features to prevent the proliferation of cracks generated during their use. One way, for example, is to fabricate the oxide from large dense particles surrounded by oxide fines and forming by hot pressing or sintering. The resultant structure, although more resistant to thermal mechanical failure, is low density and generally contains a high percentage of open pores. These were the atypical structures of the electrode and insulator material used in the US Phase I test in the USSR U-02. ^(1,2)

For MHD electrodes and insulators, these open pores act as unrestricted paths for the alkali seed, as a liquid or gas, to penetrate into the material. This transport can be substantially enhanced in a dc field.

Figure 5. Microstructural Cross Section of Some Electrode Oxides Used to Measure the Thermal Diffusivity. (As Polished)

Therefore, while the thermal shock of the oxides for the MHD electrodes and insulators of the Phase I U-02 test was improved, penetration of alkali seed into the electrodes and insulators through the open porosity (14-19 volume %) did become a factor.⁽³⁾ It would therefore be desirable to develop a ceramic with built in defects, such as pores but with the pores all closed or sealed from the surface.

Electrode materials of $0.75 \text{ Mg Al}_2\text{O}_4 \cdot 0.25 \text{ Fe}_2\text{O}_4$ have been fabricated with a high percentage of pores with essentially 100% porosity, Figures 6 and 7. At 95% of the theoretical density of 4.03 g/cm^3 , the open porosity is less than 0.01 volume %, the pores being very small. As more porosity is introduced, the open porosity increases very slightly, e.g. at 3.51 g/cm^3 or 13% porosity, the open porosity is less than 0.3 volume %. Near 80%, the pore density appears to become so high that the open porosity begins to increase substantially, Figure 6 (bottom micrograph). At 72% of theoretical density, for example, the major part of the pores are open, Figure 7.

The grain size of these controlled microstructures of spinel are large, $\sim 0.3 \text{ mm}$ in diameter. The pores are uniformly distributed throughout the oxide. This spinel also contains a second phase located at the grain boundaries. This phase contains a high concentration of Si and Ca and other impurities in addition to Mg, Al and Fe. The source of these impurities has been identified as coming from the starting powders.

The variations in porosity can be graded from one percentage to another without separation or lamination, Figure 8. Extremes such as from nearly complete open to complete closed porosity can be achieved over a very short distance. However, it must be recognized that the mechanical and thermal properties are also different.

The development of these structures is continuing in an effort to define the parameters necessary to fabricate electrodes for testing under MHD conditions and to evaluate their properties. Electrodes for

the US U-02 Phase II test will be fabricated. Attempts will also be made to utilize this technique in fabricating similar structures for other potential MHD electrode materials, i.e. $\text{CeO}_2\text{-ZrO}_2$, $\text{Y}_2\text{O}_3\text{-ZrO}_2$, $\text{FeAl}_2\text{O}_4\text{-Fe}_3\text{O}_4$ and LaCrO_3 .

3.63 g/cm³ (95% TD)
0.0 vol.% open porosity

0.1 cm

3.51 g/cm³ (90% TD)
0.1 vol.% open porosity

Figure 6. Microstructures of 0.75 Mg Al₂O₄·0.25 Fe₃O₄ with Controlled Porosity. See also Figure 7.

3.43 g/cm³ (87% TD)
0.3 vol.% open porosity

0.1 cm

3.14 g/cm³ (78% TD)
3.9 vol.% open porosity

Figure 7. Microstructures of 0.75 Mg Al₂O₄·0.25 Fe₃O₄ with Controlled Porosity. See also Figure 6.

72% TD
(~20% open porosity)

89% TD
(<0.1% open porosity)

0.02 cm

82% TD
(<3% open porosity)

87% TD
(<0.1% open porosity)

0.02 cm

Figure 8. Microstructures of $0.75 \text{ Mg Al}_2\text{O}_3 \cdot 0.25 \text{ Fe}_3\text{O}_4$
Showing Sharp Gradations of Porosity

4.2.0 Metal Current Leadout

The attachment of a metal current leadout to a ceramic electrode is a problem which must be solved. The metal and electrode must be chemically and thermally compatible with each other, e.g. similar thermal expansions are desirable, and the attachment must be maintained during use. The purpose of this study was to investigate the attachment of a variety of metals on a few ceramic electrode materials by

- fusion of the metal
- RF high rate sputtering

4.2.1 Fusion of Metal Current Leadout

The potential of coating $3 \text{ MgAl}_2\text{O}_4 \cdot \text{Fe}_3\text{O}_4$, $0.5\text{CeO}_2 \cdot 0.5\text{ZrO}_2$ and $\text{La}(\text{Mg})\text{CrO}_3$ ceramic electrode materials was investigated by fusing Ni, Cr, Cu, Ti, Fe and alloys of Ni-Cr-Fe (Nichrome and stainless steel) on the electrode at high temperatures. The surface of the small flat samples of the electrodes was cleaned and a rough surface prepared. A small amount of metal powder was sprinkled on the surface. The electrode was heated to above the melting point of the metal in a vacuum. After melting, nitrogen was introduced at temperature to 3 atmospheres in an attempt to force the molten metal into the open pores and rough surfaces of the electrode.

In all instances, the metals did not wet these ceramics, but because of the high surface tension formed small balls on the surface. These metal balls, although they show some mechanical attachment could easily be removed by rubbing the finger lightly across the surface.

Future studies will be made selecting alloys which will more easily wet the oxide surface, but will still not react extensively with the electrode. Choosing such a metal or alloy with the desirable thermal and physical properties will be the most difficult problem.

4.2.2 Sputtered Coating

Sputtered adherent coatings of metal can be applied to the ceramic electrode materials by high rate sputtering. A wide variety of metals and

alloys can be applied resulting in a strong mechanical coating of varied thicknesses. Graded coating can also be produced.

Initial coatings of nickel have been applied on $\text{CeO}_2\text{-ZrO}_2$ and $\text{MgAl}_2\text{O}_4\cdot\text{Fe}_3\text{O}_4$ electrodes. The coatings were from 0.0002 to 0.0005 cm thick and were applied uniformly over the oxide surfaces. The adherence was excellent on both the rough and smooth oxide surface, Figure 9. Thermal cycling in air to 800°C did not appear to degrade the coating. However, when heated above the melting point, the nickel was removed from most of the coated surface, forming small metal spheres.

Sputtering of electrodes with other metals and graded alloys with subsequent brazing to current leads will be studied.

5.0 Work Anticipated During Next Quarter

5.1 Characterization of Materials for US-USSR U-02 Phase II MHD Channel Test

The characterization of electrode and insulator materials for the US-USSR U-02 Phase II Channel Test will be initiated. These initial characterizations will include composition, thermal properties and microstructure.

5.2 Electrode and Insulator Fabrication

Electrodes for use in the U-02 Phase II test will be fabricated with controlled microstructures. The densities of the $3\text{MgAl}_2\text{O}_4\cdot\text{Fe}_3\text{O}_4$ will be ~89% of the theoretical with less than 0.1% open porosity.

6. Fabrication of Electrodes

Fabrication of electrodes with controlled microstructures for $\text{CeO}_2\text{-ZrO}_2$, La(Mg)CrO_3 and $3\text{FeAl}_2\text{O}_4\cdot\text{Fe}_3\text{O}_4$ will be investigated in air to 800°C did not appear to degrade the coating.

Figure 9. Sputtered nickel coating on dense (a) and porous $3\text{MgAl}_2\text{O}_4 \cdot \text{Fe}_3\text{O}_4$. The Ni coating is approximately 0.0002-0.0003 cm thick.

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