Development, Characterization and Evaluation of Materials for Open Cycle MHD

**Quarterly Report for the Period Ending
June 1978**

**J. Lambert Bates
D. D. Marchant
J. L. Daniel**

October 1978

**Prepared for the U.S. Department of Energy
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**Pacific Northwest Laboratory
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1.0 OBJECTIVES

The objectives of this program are directed toward the development and characterization of high temperature ceramics for open-cycle, coal-fired MHD power generators. The current activities are directed to electrode and insulator materials, and include (1) determination of the effects of alkali seed on the behavior of ceramics in a dc electric field; (2) development and testing of improved high temperature ceramic electrodes and insulators with controlled composition, microstructure, and properties; and (3) characterization and evaluation of materials utilized in channels being tested for MHD power generator development.⁽¹⁾

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, and seed/slag 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 including 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 EVALUATION OF METAL ELECTRODES FROM 250-HOUR MHD TEST AT AVCO

Cathodes, anodes, and slag from a metal electrode channel tested for 250 hours in the MARK VI MHD generator at AVCO, Everett, Massachusetts, (March 1978), were characterized and evaluated at Battelle, Pacific Northwest

Laboratories (PNL). The characterization included optical and electron microscopy and the scanning electron microprobe using both qualitative and quantitative EDAX.* The purpose of this evaluation was to determine the performance of the copper electrodes, specifically the platinum and nickel coated anode and copper-tungsten composite coated copper cathode. The test was conducted using an injected coal ash from the BOW, New Hampshire power plant (a high iron containing ash), Table 1. The electrodes and slag were obtained from the most electrically stressed positions of the channel. A schematic cross section of the cathode and anode are shown in Figure 1.

The anode was 7.75 mm (0.305 in.) wide with a 0.51 mm (0.020 in.) thick and 3.81 mm (0.150 in.) long platinum foil brazed to the upstream copper surface. A plate of TD nickel, 0.8 mm (0.03 in.) thick and 0.81 mm (0.32 in.) long, was also brazed with a Cu-Ag-Cd-Zn to the upstream side of the anode. A 1.5 mm (0.63 in.) wide and 1.5 mm (0.06 in.) deep groove, machined in the copper surface downstream from the Pt, was filled with a Ca stabilized-ZrO₂ castable.

The cathode was approximately twice the width of the anode, ~15.3 mm (0.60 in.). The upstream side of the cathode was also coated with TD nickel, 0.06 mm x 0.8 mm (0.025 in. x 0.03 in.), and extended to the plasma surface. A downstream top section, approximately 2 mm (0.075 in.) wide, of copper surface remained exposed to the plasma. The remaining downstream surface ~12.8 mm (~0.5 in.) was covered with 0.33 mm (0.13 in.) thick copper-tungsten metal. All were attached with the Cu-Ag-Cd-Zn braze. A nickel coating was flashed over top and side surfaces of the cathode.

Boron nitride insulators were placed between both the anode and cathode electrodes.

3.1.1 Braze

The Cu-Ag-Cd-Zn braze used to attach all coverings to the copper (both anode and cathode) electrodes was approximately 0.2 mm (0.008 in.) thick.

---

*Boron cannot be detected with the electron microprobe. Therefore, interactions involving BN insulators could only be accomplished using optical and scanning electron microscopy, and emission spectroscopy.

Figure 1. Schematic Cross Section of Cathode and Anode from AVCO 250 Hour Test

TABLE 1. Composition of Eastern Coal Ash Used During
AVCO Reference #2 250 Hour Test

<u>Oxide</u>	<u>Weight Percent</u>
P ₂ O ₅	0.58
SiO ₂	42.11
Fe ₂ O ₃	18.91
Al ₂ O ₃	23.63
TiO ₂	1.38
CaO	6.00
MgO	1.35
SO ₃	2.20
K ₂ O	2.08
N ₂ O	1.61
FeO	2.78
Fe ₂ O ₃	14.82
FeO/Fe ₂ O ₃	0.19

Large areas, 2 to 4 mm (0.08-0.16 in.) long, remained unbonded and represented 25 to 50% of the interface area (Figure 2). The areas free of voids were well bonded and remained intact during the test, with no penetration of seed, combustion products, or slag. However, erosion by combustion plasma was more intense at the exposed braze interface.

3.1.2 Anode

The upstream corner of the anode had been lost during the test resulting in an undercutting of the platinum surface, leaving the platinum protruding upstream (Figure 3). All anodes show this general characteristic. The top surface of the platinum was rippled with a "washboard" effect (Figure 4). The ZrO₂ was removed from the downstream groove and had increased substantially in both width and depth into a rounded trough. Slag had attached itself to some portions of this trough, but other areas were free of slag. The uncovered surfaces were blue in color indicating oxidation of surfaces.

Figure 3. Surface of Platinum in Contact With Plasma and Slag

Figure 2. Polished Cross Sections of Anodes After Test

Figure 4. Upstream Protrusion of Platinum

The erosion-corrosion of the braze was greater than the copper, which was greater than the TD nickel, which was more than the platinum. The leading edge of the platinum was also eroded with some evidence of melting and flow. There was no apparent alloying between the Cu, Ni, Pt, or braze in the area of erosion. A more complete description of the anode follows.

TD Nickel. Although eroded where exposed to the plasma, the TD nickel in other areas remained unchanged. No reaction, corrosion, or alloying products were observed at the nickel-braze-copper interfaces, suggesting possible arc erosion alone or corrosion-erosion which forms a volatile and/or easily eroded product, i.e., NiO. The erosion-corrosion is less than that of the braze or copper, but greater than that of platinum. In some cases, a thin layer, 1 to 10 μm (0.4×10^{-7} in.), of slag was attached to the nickel and copper (Figures 2,3). This slag was high in potassium, suggesting possible reaction between the potassium and nickel. However, no nickel could be detected in the slag.

Copper. The copper near the upstream edge eroded more than the nickel, but less than the braze. The exposed surfaces were free of any corrosion layer, but a high potassium containing slag was attached to the undercut surface of one anode. No evidence of interaction with the braze, nickel, or platinum was observed.

The entire copper surface downstream from the platinum exhibited extensive change. The original rectangular groove increased in both width and depth forming a rounded cavity 3 to 4 times the original volume. The depth was 1-1/2 to 2 times greater than the width had enlarged to include the entire width, from the Pt to the downstream edge. The castable ZrO_2 was entirely removed and/or replaced with slag.

The copper surface in this cavity appeared to have reacted electrochemically with the slag/seed, with the reaction most intense near the bottom and downstream side of the cavity. A two layered reaction product formed between the slag and copper is approximately 1 μm ($\sim 0.4 \times 10^{-4}$ in.) thick (Figure 5). The reaction product adjacent to the copper, 0.4 μm (1×10^{-5} in.) thick, is a

---

*Emission spectrochemical quantitative analyses also showed 1000 ppm Al, 200 ppm Ca, 2000 ppm Cu, 500 ppm Fe, 500 ppm Si.

Figure 5. Corrosion Layers near Bottom Copper Cavity of Copper-Slag Interface

copper oxide alloy high in potassium with some slag constituents, i.e., Mg, Al, Si, and high Ca, but depleted in iron. The outer layer near the slag, 0.3 to 0.6 μm ($0.8\text{-}1.6 \times 10^{-5}$ in.) thick, was a high copper, high potassium containing slag also depleted in iron. The slag adjacent to this latter layer was high in iron (estimated to have composition near $7 \text{M}_x\text{O}_y \cdot 3 \text{FeO}$) and contained particles of free metallic iron.

Thus, copper loss in the area of the original ZrO_2 filled cavity appears to result from the electrochemical reaction with the slag and seed and not by arc erosion. However, some arcing may occur between the copper and slag. The reducing conditions suggested by the presence of potassium and free iron metal indicate possible cathodic conditions on the downstream side of the anode.

Platinum. The upstream edge of the platinum was undercut because of the more rapid removal of braze, copper, and nickel (Figures 2,3). The leading edge of the platinum receded ~ 0.5 mm (0.02 in.) back from the original upstream edge of the anode, leaving approximately 90% of the original 0.5 mm (0.02 in.) thick platinum. The exposed upstream edge of the protruding platinum was eroded slightly underneath and the top front of this platinum protrusion indicated plastic flow or melting. The exposed surface was pure platinum and did not contain either metals of the anode construction (the boron content was less than 50 ppm*) and only minor quantities of the elements of the slag. However, near the upstream top surface, particles of slag could be found entrapped in the platinum (Figure 6). This slag was high in Si and Al, but low in Ca and Fe with some potassium. This compositional difference in the slag suggests the slag may originally have been molten along with the platinum.

The downstream edge of the platinum was rounded with slight undercutting in the area of the braze, but showed no evidence of material flow below the surface.

Slag sometimes covered the top surface of the platinum. Also, during short periods the channel was operated without slag for significant times. It is probable that the rippled surface occurred during that period when slag did not coat the Pt or upstream edge of the anode. In addition, these effects could have occurred early in the life of the electrode.

Figure 6. Slag Particles near Platinum Surface and Tip Exposed to Plasma.

Slag. Very little slag remained attached to the platinum surface or to the TD nickel (Figure 2,3). Smaller particles of slag were entrapped in platinum near upstream plasma surface (see previous discussion). Often slag was found in the upstream cavity of the anode near the erosion area of the Cu, Ni, and below the Pt (Figure 4). However, the major amount of slag was found on the platinum surface and in the enlarged downstream machined groove originally filled with CaO stabilized ZrO₂.

The composition and structure of the slag varied depending upon its location on the anode. The slag immediately above the platinum was a two-phase oxide containing two types of spherical metal particles (Figure 7). The slag matrix in this area (grey color) is a potassium aluminosilicate, K₂O·Al₂O₃·2SiO₂, with only a trace of iron, titanium, copper (Area A, Figure 7A). The lighter second phase is a potassium calcium silicate, possibly a fine mixture of 3CaO·2SiO₂ and K₂O·2SiO₂ with only smaller quantities of aluminum (3.6 mole%), magnesium (1.7 mole%), titanium (1.1 mole%) and iron (2.8 mole%) (Area A, Figure 7A).

The large spherical metal particles are a platinum-iron alloy with minor quantities of copper and nickel (Figure 7B). The smaller, less spherical metal particles vary only slightly in composition from the large metal spheres.

The slag, Figure 8, immediately downstream from the platinum had only minor oxide second phase, but had large pores with two types of metal phases, Figure 8, Area A, and Figure 9A. The larger of these particles, ~14 μm (~0.55 x 10⁻³ in.) is a high platinum, low copper alloy with some iron. The smaller metal particles, ~7 μm (0.26 x 10⁻³ in.) in diameter, are high in copper and low in platinum with traces of iron.

The microstructure of the slag downstream from the platinum and immediately over the original ZrO₂ filled groove varies with the distance from the plasma surface (Figure 8). The slag at the plasma surface is glassy, single phase showing evidence of flow and rapid cooling, (Figure 8, Area C). Immediately below this is a mottled, two phase

a b

c d

Figure 7. Microstructure of Coal Slag Above Platinum Showing Two Phase Structure (a) and Metal Particles (b).

Figure 8. Slag Above Cavity in Copper.

A

B

Figure 9. Microstructure of Area B in Figure 8 Showing Slag A and Metal Particles B.

region which contains irregularly shaped small pores and irregularly shaped metal particles (Figure 10). These particles ($\sim 13 \mu\text{m}$ diameter) are iron with traces of potassium, copper, silicon, and aluminum. About midway to the copper is the two-phase oxide slag region, Area B, Figure 8, with areas containing many small metallic particles (Figure 11). The large particles, $\sim 4 \mu\text{m}$ in diameter, are primarily iron and potassium with smaller amounts of Mg, Al, Si, Ca, and a trace of Ti and Cu. The many smaller particles are principally Pt, Cu, and Fe with significant amounts of K and Ni and smaller amounts of Al and Si.

As described earlier, the slag adjacent to the copper, Area B, Figure 8, contains free iron particles and the oxide slag is depleted in iron.

The source of the platinum metal particles in the slag appears to be the molten platinum coating with iron additions reduced from the slag. The copper source is probably the arc eroded upstream edge of the anode. In contrast, the iron metal particles appear to result from cathodic reduction of the iron containing slag, some of which have alloyed with the other Pt or Cu metal particles.

Boron Nitride. The BN insulator had eroded at the top surface into an unsymmetrical point (less on the upstream than the downstream side). Most of the insulators had fractured $\sim 1 \text{ mm}$ below the surface. The remaining BN was the same structurally as that of the starting BN. Only minor amounts of potassium were found on the pores of the insulator near the surface exposed to the plasma.

3.1.3 Cathode

The cathode experienced little change compared to the anode (Figures 12 and 13). The upstream edge of the cathode had eroded away, back to the copper-tungsten which covered the downstream top surface of the cathode. This included both the TD nickel and the copper. The slag which had adhered to the cathode was easily removed in pieces before evaluation.

Figure 10. Microstructure of Slag from Area D, Figure 8, Showing Fe Second Phase.

A

B

Figure 11. Microstructure of Anode Slag Midway Between Plasma Surface and Copper, Area C (Figure 8).

Figure 12. Cross Sections of Cathodes After 250-Hour MHD Test.

Figure 13. Cross Sections of Cathodes After 250-Hour MHD Test.

Nickel Coating. The 0.03 mm (~ 0.0012 in.) thick coating of nickel, which had been flashed on the sides and top of the cathode, was still intact on the copper, TD nickel surface, and the Cu-W which were on the sides of cathode (Figure 14A). However, on the surface of the Cu-W exposed to the plasma, much of the nickel coating had broken off from the surface leaving an apparent thin oxidizing layer. Those sections of the nickel coating remaining were reduced in thickness to approximately 0.02 mm (0.0008 in.) and contained a series of vertical cracks [~ 0.04 mm (0.0016 in.)]. These cracks were approximately one-half the remaining coating thickness. The top half also appeared to have altered structure. These effects may be related to the magnetic transition which occurs at 353°C and annealing which also occurs between 350-400°C.

TD Nickel. The TD nickel eroded to depths from 2 to 5 mm (0.08 to 0.2 in.). The erosion or corrosion appeared to be greater than the copper. Attack at the braze was more intense than at the nickel.

Copper. The copper edge, which was exposed to the upstream plasma surface, was degraded to an approximate 45° angle down to the top of the remaining TD nickel. The top surface recessed to approximately 1/4 to 3/4 the thickness of the Cu-W plate. The surface was free of corrosion and was unalloyed.

Copper-Tungsten. The Cu-W was not an alloy, but a bonded composite of Cu and W particles. The Cu-W surface plates eroded only on the upstream, top corner, and leading edge after the copper and nickel had been removed. The less the copper removal, the less the erosion of the Cu-W. Conversely, the downstream edge and copper corner were unchanged. The Cu-W surface is slightly oxidized, even under the Ni surface coating.

Boron Nitride. The Bn insulators had fractured ~ 3.5 -5 mm (0.14-0.20 in.) below the cathode surface (Figures 12-13). Because of this, portions of the top sections of the BN were missing or displaced. For those insulators which remained, ~ 1 -2 mm (0.04-0.08 in.) of the top was lost, (Figure 15). This degradation was not uniform, being greatest on the downstream side, giving the appearance of two unsymmetrical points. This suggests erosion and corrosion by the combustion plasma. The top exposed

Figure 14. Nickel Coating Remaining on (A) Side of Cu-W and (B) Top of Cu-W.

Figure 15. Top Surfaces of Boron Nitride Insulators Showing Reactions At Surface.

surfaces had reacted with the potassium seed to depths up to 1 mm which probably added to the removal of the top surface. Penetration and retention of seed is greatest along open pores. It could not be determined if the potassium had reacted with the BN.

Slag. The slag was easily removed in sections from the cathode surfaces. Attachment was greatest near the boron nitride insulators, especially those areas in which the insulator surface apparently cracked and was lost. The slag was more friable than that deposited on the anode, especially near the cathode surface. The porosity was very high.

The surface was generally friable and although it had the appearance of once being molten, it was crazed with fractures near the surface, (Figure 16).

The oxide slag is three phase (Figure 16), with a darker continuous matrix with composition identical to that of the anode slag, i.e. $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ with traces of iron and titanium. The lighter second phase is a $CaO \cdot 2SiO_2$ with ~6 mole% iron and minor amounts of Ti, Al and Mg. This phase is located near the plasma surface where the temperature is greatest. Nearer the cathode surface, $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ phase increases with decreasing amounts of calcium.

The slag also contains irregularly shaped free iron metal particles which are found in the center of the slag layer. The iron particles are larger nearest the plasma surface.

3.1.4 Conclusions

Boron Nitride

- Did not interact with slag or metal electrodes.
- Exposed surface eroded and/or vaporized.
- Top surface of cathode BN insulator reacted with potassium seed.
- BN plates fractured below plasma surface.

Figure 16. Microstructure of Slag Coating Cathode Electrodes.

Slag

- Potassium seed reacted with slag forming a $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ matrix phase. The CaO in slag forms a $xCaO \cdot ySiO_2$ second phase with major amounts of iron, aluminum, magnesium and titanium. Second phase separation occurs in higher temperature regions of slag.
- Slag on cathode contains more potassium than slag on anode and has large quantities of free iron metal present.
- Slag had reacted with anode, especially on upstream portion of anode in the cavity originally containing CaO stabilized ZrO_2 .
- Slag on anode varies in composition and structure along surface of anode with slag on downstream portions of the anode showing cathodic reduction, free iron and electrochemical reactions.
- The slag examined on both anode and cathode appeared to have been on electrode surfaces for some period of time.

Anode

- The erosion of anode probably occurred early in test life.
- Deterioration of upstream edge resulted from erosion due primarily to arcing and flow of combustion gases/slag plasma, causing undercutting of Pt coating. Corrosion may be factor. Degree of erosion dependent upon metal hardness and/or oxidation resistance, braze > copper > nickel > platinum.
- Melting and flow of platinum forming the washboard surface appears to result from melting of platinum and not alloying with the Cu, Ni or bronze from electrode, the iron in the slag or boron from the insulator. The high temperature necessary for melting apparently occurred during clean fuel operation (non-slagging) from arcing and partial loss of heat transfer.
- The concentration of arcing and current flow on the upstream edge of anodes results in cathodic and reducing conditions on downstream portions of electrode and slag.

- Degradation of downstream copper in areas of original ZrO_2 filled groove results from electrochemical corrosion.
- Attachment of slag to anode appears to be mainly mechanical.

Cathode

- Only minor upstream edge erosion, primarily on Ni and Cu.
- Cu-W degraded very little with only surface reaction layer.
- No reactions with slag.

3.2 CHARACTERIZATION AND PROPERTIES OF USSR MgO INSULATING WALL MATERIAL

An MgO used by the USSR as their MHD insulator wall has been characterized and properties evaluated. The insulator is MgO (96.7 mole%) and contains minor amounts of calcium (1.3 mole%), silicon (1.7 mole%) and iron (0.3 mole%). The insulator is made up of large, high density fused particles 0.4 to 1.0 mm in diameter surrounded by fines which have sintered and bonded to the larger grains, (Figures 17 and 18). The larger grains are MgO with a trace of iron and silicon (<1 mole%). The smaller grains are also nearly pure MgO , but are bonded with a second phase. This second phase has a composition near $3\text{MgO} \cdot 3\text{SiO}_2 \cdot 4\text{CaO}$ and is concentrated in pockets surrounding these smaller MgO grains. This insulator structure is very similar to that for periclase used in making commercial refractories for BOP brick.⁽²⁾ The composition is similar to a 94% dense P-6 grain which is 97% MgO , 1.3% CaO , 1.0% SiO_2 , 0.2% Fe_2O_3 , and 0.2% Al_2O_3^* with CaO/SiO_2 ratio of 1.3. From the phase diagram,⁽³⁾ this composition melts near 2075K. The shape of this second phase also suggests a molten phase during fabrication.

In the pores among the smaller particles and the second phase grain boundaries are found small residual amounts of Si, P, Cl and Zn, suggesting the use of a binder during fabrication.

Some spherical particles (up to 0.4 mm in diameter) were found in some pure MgO grains, generally near grain boundaries (Figure 18). These particles are composed of three different phases.

---

*Mole percent.

Figure 17. Microstructure USSR MgO Insulator.

Figure 18. Microstructure USSR MgO Insulator.

- A. 66% CaO, 32% SiO₂ and 2% MgO*
- B. 50% CaO, 37% SiO₂ and 13% MgO*
- C. 49% CaO, 27% SiO₂ and 24% MgO*

These particles appear to be residual from the original fused grain.

The areas with rounded MgO particles (0.1 mm diameter) also have a second phase at their grain boundaries, Figure 18. The larger grains are MgO with traces of Si, Ca and Fe, similar to those of the large, more irregularly shaped MgO grains. The second phase, which occurs in the spaces between grains is 11% MgO, 34% SiO₂ and 55% CaO.* This phase composition melts near 2025K.

3.2.1 Electrical Resistivity

The dc electrical resistivity was measured in air using a three contact guard ring technique. These results are illustrated in Figure 19. The log σ versus K^{-1} does not appear linear, although it approaches a linear relationship above 1000K. The data at higher temperature above 900K agrees with previously reported electrical conductivity reported by Telegin et al.⁽⁴⁾ However, these latter two sets of data were illustrated graphically and these data summarized here were estimated from those graphs.

The values are 1 to 5 orders of magnitude higher than values reported for single crystal MgO,⁽⁵⁾ (see also original references 6-8) also measured in air, Figure 20.

Only below ~525K does the conductivity values appear to vary with the time of applied current, where the values at 10 minutes are lower than at 1 minute. This suggests polarization and ionic conductivity since platinum blocking electrodes were used.

3.2.2 Thermal Diffusivity/Conductivity

The thermal diffusivity was measured in argon using a flash pulse technique, Figure 21. The thermal conductivity was calculated from reported heat capacity data, measured room temperature data and thermal expansion values, Figure 22. The scatter in the data was unusually large, with higher

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*Mole percent

Figure 19. Electrical Conductivity of USSR MgO (Direct Current Measurements Taken One and Ten Minutes After Application of Electric Field).

Figure 20. Summary of Electrical Conductivity Data for MgO. See Reference 5 of Text. Data Lines 2, 9, and 10 are References 6, 7, and 8 respectively.

Figure 21. Thermal Diffusivity of USSR MgO Insulator.

Figure 22. Thermal Conductivity of USSR MgO Insulator.

values on cooling than during the initial heating. For all data, the thermal diffusivity (α) can be expressed as

$$\alpha = (2.403 \times 10^5 + 4.908 \times 10^3 K)^{-1} m^2/sec$$

with coefficient of determination $r^2 = 0.89$. The values on heating (α_H) and cooling (α_C) are:

$$\alpha_H = (5.580 \times 10^5 + 4.931 K)^{-1} m^2/sec \quad (r^2 = 0.92)$$

and

$$\alpha_C = (9.178 \times 10^4 + 4.679 \times 10^3 K)^{-1} m^2/sec \quad (r^2 = 0.93),$$

respectively.

The average thermal conductivity values for all data can be expressed as

$$\lambda = (7.717 \times 10^{-3} + 1.256 \times 10^{-2} K)^{-1} W/mK$$

with $r^2 = 0.90$ (see Figure 22).

The thermal conductivity/diffusivity values are about 40% higher than the data reported for a similar MgO insulator,⁽⁴⁾ Figure 23, but less by ~40% at low temperatures and by 90% at high temperatures than that for MgO electrode insulators prepared by hot pressing in the U.S.⁽⁹⁾

3.3 THERMAL DIFFUSIVITY/THERMAL CONDUCTIVITY

The thermal diffusivity has been measured and thermal conductivity calculated for the electrode and insulator materials tested in the USSR U-02 Phase III. This included the materials evaluated in the preliminary proof tests conducted in the Westinghouse materials test facility.⁽¹⁰⁾ In the course of these investigations it was observed that there were differences between the measured diffusivities of the proof test electrode materials and those used in the U-02 Phase III test. This was especially evident in the $0.7La_{0.95}Mg_{0.05}CrO_3 \cdot 0.30 [0.12Y_{2O_3} \cdot 0.88ZrO_2]$ and $La_{0.95}Mg_{0.05}CrO_3$ electrodes.

These differences, up to 30%, were significant since the data for the design of the U-02 Phase III test was that obtained for the materials used in the Westinghouse proof tests. The thermal conductivities for the materials measured for the proof tests were higher than those of the U-02

Figure 23. Thermal Resistivity of USSR Mgo Insulator.

Phase III materials. However, the later samples were not made available for thermal diffusivity measurements until after the design of U-02 Phase was completed and construction initiated. This generally resulted in operating electrode surface temperatures lower than predicted.

The electrodes used in the Westinghouse proof tests and U-02 Phase III had been heat treated differently after hot pressing and before assembly in the U.S. module. The proof test electrodes were heated in air at 1475K for four hours while the U-02 Phase III materials, although fabricated the same, were heated in oxygen for eight hours at 1775K.

To clarify potential differences in the thermal diffusivities and conductivities resulting from these heat treatments, the thermal diffusivities of the as hot-pressed, the air-1475K annealed, and the O_2 -1775K annealed samples for each of these two electrode material types were measured in argon. These results were analyzed and the data compared with previous measurements. The samples were obtained from the same hot-pressed billet and from as near the same part of the billet as possible. Heat treating was performed at Westinghouse under the same conditions as those performed for the electrodes used in the proof tests and the U-02 Phase III test. The results for the $La(Mg)CrO_3$ are reported here. Evaluation of the $La(Mg)CrO_3 + ZrO_2$ results are not yet complete.

3.3.1 $La_{0.95}Mg_{0.95}CrO_3$

The thermal diffusivity/conductivity for the proof tests were originally assumed to be the same as that measured previously for the USSR U-02 Phase II test,^(9,12) Figures 24 and 25. The data for the proof test are also illustrated in Figure 26 and are tabulated in Tables 2 and 3. [Two different groups of chromite electrodes were used in the Phase III U-02 test, M-123A M-124]. Also included are data for another sintered chromite provided by another supplier,* Table 4. The data for the chromite measured after the tests, before (M-137a) and after heat treatment (M-138A and M-139A) are summarized in Figures 27 and 28 and Tables 5, 6, and 7.

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*A. T. Research

Figure 24. Thermal Diffusivity of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ (w)

Figure 25. Thermal Conductivity of U-02 Phase II $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$.

Figure 26. Thermal Diffusivity of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ Used in US-USSR U-02 Phase III Tests, M-123A and M-124A Plus ATR Sintered Chromite

Figure 27. Thermal Diffusivities of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ Measured as a Function of Heat Treatment, Compared to As Hot Pressed M-137A.

Figure 28. Summary of Thermal Conductivities of La_{0.95}Mg_{0.05}CrO₃ as a Function of Heating and Cooling.

TABLE 2. BNW DATA SHEET: Thermal Diffusivity/Conductivity

Material: $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ [M-123A]

Source: Westinghouse Research Laboratory

Fabrication: Hot pressed, 1923K at 27.6 MPa (4000 psi) in N_2 ; graphite diesHeat Treatment: O_2 at 1773K for 8 hoursDensity: 6.39 g/cm^3 (98% T,D)

Structure: Mostly single phase with small second phase high in Mg and Cr

Property Data:

Temperature K	Thermal Diffusivity $\text{m}^2/\text{sec}(10^{-7})$	Thermal Conductivity Watts/m-K
505	0.01337	0.0426
617	0.01246	0.0407
716	0.01371	0.0456
829	0.01514	0.0512
928	0.01598	0.0546
994	0.01521	0.0522
1080	0.01439	0.0499
1177	0.01250	0.0437
1279	0.01099	0.0387
1394	0.00972	0.0315
1494	0.00890	0.0319
1589	0.00791	0.0285
1676	0.00807	0.0292
1775	0.00849	0.0310
1883	0.00766	0.0282
1761	0.00857	0.0313
1648	0.00792	0.0286
1564	0.00805	0.0289
1466	0.00901	0.0322
1365	0.00930	0.0330
1257	0.01012	0.0356
1160	0.00941	0.0328
1058	0.01001	0.0346
961	0.00982	0.0336
765	0.00946	0.0317
671	0.00937	0.0311
526	0.00992	0.0318

(1) Measurements made in argon

(2) Thermal expansion measured $\Delta L/L = 8.8 \times 10^{-6} \times \Delta T$ (3) Specific heat data calculated using reported C_p values⁽¹¹⁾ for oxides of La_2O_3 , MgO and Cr_2O_3 using Knoop-Neumann theory for mixtures.

TABLE 3. BNW DATA SHEET: Thermal Diffusivity/Conductivity

Material: $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ [M-124]

Source: Westinghouse Research Laboratory, U-02, Phase III, Group 4

Fabrication: Hot pressed at 20.7 MPa (3000 psi) at 1923K for 2.5 hours
in N_2 ; graphite diesHeat treatment: O_2 at 1773K for 8 hoursDensity: 6.39 g/cm^3 (98% TD)

Structure: Single phase with small second phase high in Cr and Mg

Property Data:

Temperature K	Thermal Diffusivity ⁽¹⁾ $\text{m}^2/\text{sec}(10^{-7})$	Thermal Conductivity Watts/m-K
639	11.63	4.48
714	11.22	4.38
931	11.86	4.75
1026	8.99	4.49
1142	9.56	3.92
1214	10.99	4.52
1305	9.04	3.75
1389	7.12	3.00
1490	6.58	2.77
1594	6.15	2.61
1686	6.00	2.56
1789	7.24	3.12
1886	6.14	2.66
1827	6.26	2.67
1746	6.24	2.67
1659	6.66	2.84
1561	7.24	3.06
1451	7.37	3.10
1254	7.53	3.11
1148	7.21	2.93
1013	8.35	3.37
818	9.19	3.64
733	9.15	3.58
650	10.04	3.88
525	10.93	4.11

(1) Measurements made in argon

(2) Thermal expansion measured $\Delta L/L = 8.8 \times 10^{-6} \Delta T$ (3) Specific heat data calculated using reported C_p values⁽¹¹⁾ for oxides of La_2O_3 , MgO and Cr_2O_3 using Knoop-Neumann theory for mixtures.

TABLE 4. BNW DATA SHEET: Thermal Diffusivity/Conductivity

Material: $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$

Source: A. T. Research

Fabrication: Sintered in [$\text{Po}_7 = 10^{-10} - 10^{11}$ atm] 1975K

Heat Treatment: 1823K in air

Density: 6.15 g/cm^3 (94% TD)

Property Data:

Temperature K	Thermal Diffusivity ^(1,2) $\text{m}^2/\text{sec} (10^{-7})$	Thermal Conductivity ^(2,3) Watts/m-K
533	9.83	3.49
618	9.67	3.50
733	6.58	2.43
823	9.33	3.49
903	8.01	3.03
1043	9.44	3.60
1118	8.28	3.18
1238	7.03	2.73
1338	8.38	3.29
1433	6.14	2.42
1538	6.29	2.50
1663	5.91	2.37
1758	6.27	2.53
1873	6.26	2.55
1763	6.09	2.46
1673	6.24	2.51
1526	6.35	2.52
1445	6.10	2.41
1362	6.43	2.52
1252	6.60	2.56
1154	6.81	2.62
1045	7.02	2.68
941	6.94	2.63
833	7.85	2.94
693	8.82	3.241
630	8.80	3.20
538	9.81	3.49

(1) Measurements made in argon

(2) Thermal expansion measured $\Delta L/L = 8.8 \times 10^{-6} \times \Delta T$

(3) Specific heat data calculated using reported C_p values⁽¹¹⁾ for oxides of La_2O_3 , MgO , and Cr_2O_3 using Knoop-Neumann theory for mixtures.

TABLE 5. BNW DATA SHEET: Thermal Diffusivity/Conductivity

Material: $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ [M-137A]

Source: Westinghouse Research Laboratory (LC-TT-305)

Fabrication: Hot pressed at 20.7 MPa (3000 psi) for 2.5 hrs at 1923K
in N_2 ; graphite dies

Heat Treatment: None

Density: 6.60 g/cm^3 (before measurements)

Structure:

Property Data:

Temperature K	Thermal Diffusivity $\text{m}^2/\text{sec}(10^{-7})$	Thermal Conductivity Watts/m-K
586	21.88	8.68
759	13.94	5.67
916	10.62	4.39
1027	8.495	3.54
1150	7.660	3.23
1256	6.802	2.89
1344	6.484	2.77
1435	5.826	2.50
1522	5.963	2.57
1610	5.631	2.44
1690	6.221	2.71
1762	5.585	2.44
1689	6.095	2.65
1602	5.476	2.37
1511	5.439	2.35
1425	5.983	2.57
1327	5.909	2.52
1210	6.125	2.62
1106	6.757	2.84
1008	6.881	2.87
893	7.133	2.94
794	7.481	3.06
706	8.039	3.25
592	8.939	3.55
491	9.561	3.71

After heat treatment 490-1690K:

$$\alpha^{-1} = 8.130 \times 10^5 + 6.140 \times 10^2 \text{K} \quad (r^2 = 0.90)$$

$$\lambda^{-1} = 0.2312 + 11.13 \times 10^{-5} \text{K} \quad (r^2 = 0.87)$$

- (1) Measurements made in argon
- (2) Thermal expansion measured $\Delta L/L = 8.8 \times 10^{-6} \times \Delta T$
- (3) Specific heat data calculated using reported C_p values⁽¹¹⁾ for oxides of La_2O_3 , MgO and Cr_2O_3 using Knoop-Neumann theory for mixtures.

TABLE 6. BNW DATA SHEET: Thermal Diffusivity/Conductivity

Material: $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ [M-138-A]

Source: Westinghouse Research Laboratory (LC-TT0305)

Fabrication: Hot pressed at 20.7 MPa (3000 psi) at 1923K for 2.5 hours
in N_2 ; graphite dies

Heat Treatment: Air at 1473K for four hours

Density: 6.57 g/cm^3 (before measurements)

Structure:

Property Data:

Temperature K	Thermal Diffusivity ^(2,3) $\text{m}^2/\text{sec} (10^{-7})$	Thermal Conductivity ^(2,3) Watts/m-K
441	13.12	5.01
574	10.23	4.04
765	8.770	3.56
919	8.033	3.31
1054	7.599	3.16
1169	7.018	2.95
1272	6.635	2.81
1356	6.295	2.68
1438	5.902	2.52
1542	5.949	2.56
1659	5.872	2.54
1757	5.665	2.47
1697	5.144	2.23
1620	5.334	2.31
1525	5.426	2.33
1437	5.621	2.40
1340	5.796	2.46
1225	6.032	2.54
1123	6.243	2.63
486	9.339	3.60
672	7.745	3.10
827	7.371	3.01
962	7.365	3.04
1094	6.593	2.75
1197	6.156	2.59

After heat treatment 486-1697K:

$$\alpha^{-1} = 7.652 \times 10^5 + 7.026 \times 10^2 \text{K} \quad (r^2 = 0.98)$$

$$\lambda^{-1} = 0.2327 \times 10^5 + 12.19 \times 10^{-5} \text{K} \quad (r^2 = 0.90)$$

- (1) Measurements made in argon
- (2) Thermal expansion measured $\Delta L/L = 8.8 \times 10^{-6} \times \Delta T$
- (3) Specific heat data calculated using reported C_p values⁽¹¹⁾ for oxides of La_2O_3 , MgO and Cr_2O_3 using Knoop-Neumann theory for mixtures.

TABLE 7. BNW DATA SHEET: Thermal Diffusivity/Conductivity

Material: $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ [M-139-A]

Source: Westinghouse Research Laboratory (LC-TT0305)

Fabrication: Hot pressed at 20.7 MPa (3000 psi) at 1925K for 2.5 hrs
in N_2 ; graphite dies

Heat Treatment: O_2 at 1773K for 8 hrs

Density: 6.50 g/cm^3 (99%TD) before treatment

Structure:

Property Data:

Temperature K	Thermal Diffusivity ⁽¹⁻²⁾ m^2/sec	Thermal Conductivity ⁽²⁻³⁾ Watts/m^2
487	9.962	3.80
683	8.559	3.40
828	8.482	3.42
978	7.488	3.06
1104	6.848	2.83
1189	6.602	2.75
1301	6.436	2.70
1405	5.911	2.49
1496	5.933	2.52
1614	5.589	2.39
1718	5.521	2.37
1784	5.640	2.43
1695	5.440	2.33
1612	5.457	2.33
1523	5.551	2.36
1423	5.802	2.45
1326	6.096	2.56
1203	6.261	2.61
1108	6.544	2.71
1002	6.636	2.72
848	7.162	2.90
702	7.657	3.05
612	7.980	3.13
520	8.791	3.38

On heating (487-1784K)

$$\alpha^{-1} = 7.092 \times 10^5 + 6.483 \times 10^2 \text{K} \quad (r^2 = 0.97)$$

$$\lambda^{-1} = 0.2008 + 13.20 \times 10^{-5} \text{K} \quad (r^2 = 0.97)$$

On cooling (520 to 1784K)

$$\alpha^{-1} = 8.688 \times 10^5 + 6.032 \times 10^2 \text{K} \quad (r^2 = 0.99)$$

$$\lambda^{-1} = 0.2578 + 9.959 \times 10^2 \text{K} \quad (r^2 = 0.94)$$

- (1) Measurements made in argon
- (2) Thermal expansion measured $\Delta L/L = 8.8 \times 10^{-6} \times \Delta T$
- (3) Specific heat data calculated using reported C_p values⁽¹¹⁾ for oxides of La_2O_3 , MgO and Cr_2O_3 using Knoop-Neumann theory for mixtures.

M-123A was the ZrO_2 free portion of a graded $\text{ZrO}_2\text{-La(Mg)CrO}_3$ composite. The M-124A sample was from an all $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ hot-pressed billet. The latter billet was hot-pressed at 20.7 MPa compared to 27.6 MPa, although both exhibited the same density and were reported to have been heat treated in an identical manner.

The M-137A, M-138A and M-139A samples were obtained from the same compact, and cut from adjacent parts of the hot-pressed billet. Only the heat treatment differs.

The thermal diffusivity and thermal conductivities of the M-137A, M-138A and M-139A, which differs only from heat treatment conditions underwent change on annealing to temperatures greater than 1750K, the largest for that of the as-received, hot pressed chromite, Figures 27 and 28.

The thermal diffusivity of the $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ used in the channel of the USSR-US U-02 Phase III test exhibit anomalies between 600 and 1000K. The diffusivities also undergo a permanent decrease above 1000K, with the data below 1400K lower on cooling. The cause of these variations and differences between samples is not known.

Heat treatment in air, oxygen, or the reducing condition in argon during the thermal diffusivity measurements all result in lower values. After heat treatment to 1750K or greater, the values on cooling and subsequent heating (M-138A) are essentially the same within experimental error, as indicated in the linear plot of the thermal resistivity versus temperature, Figure 29.*

The data on cooling for the M-137A, 138A and 139A fit the following equations:

$$\begin{aligned} \text{M-137A} \quad \alpha^{-1} &= 8.130 \times 10^5 + 6.140 \times 10^2 \text{K} \quad (r^2 = 0.90) \\ \lambda^{-1} &= 0.2312 + 11.13 \times 10^{-5} \text{K} \quad (r^2 = 0.87) \\ \text{M-138A} \quad \alpha^{-1} &= 7.652 \times 10^5 + 7.026 \times 10^2 \text{K} \quad (r^2 = 0.98) \\ \lambda^{-1} &= 0.2327 + 12.19 \times 10^{-5} \text{K} \quad (r^2 = 0.90) \end{aligned}$$

* α in m^2/sec and λ in watts/m-k

Figure 29. Thermal Resistivities of La_{0.95}Mg_{0.05}CrO₃ After Heat Treatment.

$$\begin{array}{l} \text{M-139A} \\ \text{(cooling)} \end{array} \quad \alpha^{-1} = 8.688 \times 10^5 + 6.032 \times 10^2 \text{K} \quad (r^2 = 0.99)$$

$$\lambda^{-1} = 8.688 \times 10^5 + 6.032 \times 10^2 \text{K} \quad (r^2 = 0.99)$$

For all data for M-137A, M-138A and M-139A, on cooling:

$$\alpha^{-1} = 7.841 \times 10^5 + 6.759 \times 10^2 \text{K} \quad (r^2 = 0.975)$$

$$\lambda^{-1} = 0.2401 + 11.14 \times 10^{-5} \text{K} \quad (r^2 = 0.88)$$

The variation between samples on cooling may be related to differences in density. Although it does not vary linearly, the thermal conductivity increases with increasing density. For example, at 800K, $\lambda = 3.12, 3.03,$ and 2.96 watts/M-k for M-137A, M-138A, and M-139A which have measured densities of $6.60, 6.57,$ and 6.50 g/cm^3 , respectively.

The thermal diffusivities and conductivities of these controlled heat treated samples (M-137A, M-138A and M-139A) on cooling are: (1) 0 to 20% higher than the values for $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ used in the Phase III test, Figure 26, with the maximum variation near 1200K, and (2) 0 to 25% lower than that for the U-02 Phase III samples M-123A and M-124.

The recommended data for evaluating the design and performance of the Phase III test of the US module in the USSR's U-02 is probably the M-139A data on heating since it is the heat treatment used. The variations between $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ samples can vary depending upon heat treatment time and temperature, and appears independent of the heat treatment atmosphere. The variations between samples after maximum heat treatment probably are due to compositional (e.g., second phases) and structural (e.g., crack) differences. The variations due to density are small. It is, therefore, necessary when using $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ as an MHD electrode to consider the potential variations between samples and the effects of heat treatment.

3.4 COPRECIPITATION OF CERAMICS POWDERS

Proper screening tests of ceramic compositions for potential MHD electrodes and insulators require that the materials be fabricated with adequate chemical microstructural (uniformity of composites and phase distribution, porosity, grain size, etc.) properties. If the properties are not reproducible, screening is difficult for variations may be due to fabrication differences instead of specific compositional or test differences. A fabrication technique has been used that produces ceramic oxides with uniform composition and with reproducible controlled microstructures. The technique consists of coprecipitating acid solutions of the chemical components through neutralizing the acid solutions with bases. The coprecipitate is treated with organics to remove excess water and dried. The powder is then calcined for fabrication by cold pressing and sintering. Densities to 98% of the theoretical density are obtainable with controlled times, temperatures and sintering atmospheres. The resultant sintered oxides have porosity along the grain boundaries of equiaxed grains. The technique has been successfully used to fabricate a variety of rare earth doped hafnates and zirconates. All of the chemical species precipitated simultaneously during acid neutralization. The resulting sintered oxides were homogeneous in composition as determined by random analysis using ceramography and energy dispersive x-ray analysis technique (EDAX) on the scanning electron microscope (SEM). The crystal structure was also determined by x-ray diffraction. Not all of the compositions were single phased but the phases identified seem reasonable to those areas predicted by phase equilibrium. For most compositions, the phase equilibria data are non-existent; therefore, equilibria must be estimated by extrapolation from known compositions of analogous compounds with similar chemical properties. In many of the coprecipitations involving hafnia, the cubic stabilized structure developed during the calcining at 1373K.

3.5 PROPERTIES OF YTTRIA CHROMITES

Yttrium chromite may be a good substitute for lanthanum chromite in MHD electrode applications. Unlike the lanthanum chromite, yttrium chromite does not result in the formation of hygroscopic decomposition products, e.g. La_2O_3 . The melting points⁽¹⁾ of the analogous yttrium chromite are 100 to 200K lower than corresponding lanthanum chromite compositions. The thermal expansion of several yttrium chromites along with two lanthanum chromite samples are given in Table 8. Yttrium has a slightly lower thermal expansion coefficient than the corresponding lanthanum chromite.

The electrical conductivity of several yttria compositions, measured using a four point technique, are shown in Figure 31. All of the yttria samples showed no polarization at current densities to 0.1 amp/cm^2 , indicating mostly electronic conduction. In a reduced state, i.e., when the samples are greenish in color instead of brownish-black, the electrical conductivity is about an order of magnitude lower with a higher temperature dependence.

Several electrochemical tests were conducted on both yttrium and lanthanum chromite. A summary of the test results are shown in Table 9. Preliminary results indicate that the yttrium chromites are more resistant to corrosion than the corresponding lanthanum chromites. Examination of the yttria chromites has not been completed but will be included in the later reports. No hydration except that caused by the potassium seed was observed following testing of the yttria chromite after being exposed to ambient air for two weeks. In contrast, some of the lanthanum chromites began to hydrate within two hours after exposure to ambient atmosphere conditions. The hydration is partially due to lanthanum oxide, a hydroxide or carbonate.

3.6 RARE EARTH HAFNATES

Due to very promising results with some preliminary electrochemical corrosion in coal slag on rare earth doped hafnium oxide, several different

TABLE 8. Thermal Expansion of Yttrium and Lanthanum Chromites

<u>Composition</u>	<u>Thermal Expansion Coefficient, °K⁻¹ 373-1673 K (10⁻⁶)</u>
$\text{Y}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$	7.4
$\text{YMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$	8.7
$\text{YMg}_{0.1}\text{Cr}_{0.9}\text{O}_3$	8.8
$\text{YMg}_{0.2}\text{Cr}_{0.8}\text{O}_3$	8.8
$\text{Y}(\text{Mg}_{0.05}\text{Cr}_{0.95})_{0.75}\text{Al}_{0.25}\text{O}_3$	8.4
$\text{Y}(\text{Mg}_{0.05}\text{Cr}_{0.95})_{0.85}\text{Al}_{0.15}\text{O}_3$	8.8
$\text{Y}(\text{Mg}_{0.05}\text{Cr}_{0.95})_{0.05}\text{Al}_{0.5}\text{O}_3$	8.6
YAlO_3	8.8
$\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$	9.5
$\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$	9.4
$\text{Y}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$	8.3
$\text{Y}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$	10.6
$\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$	9.5
$\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$	8.8

TABLE 9. Electrochemical Testing of Both Yttrium and Lanthanum Chromites

Test	Compound	Electrolyte	Temp., °K	Current Density, A/cm ²	Corrosion, μ g/Coulomb	
					Cathode	Anode
160	YMg _{0.05} Cr _{0.95} O ₃	K ₂ SO ₄	1373	1.0	<10	<10
158	YMg _{0.05} Cr _{0.95} O ₃	Illinois #6 + 10 mole% K ₂ O	1723	0.8	14	7
167	Y(Mg _{0.05} Cr _{0.95}) _{0.75} Al _{0.25} O ₃	Montana Rosebud + 10 mole% K ₂ O	1723	1.0	15	<31
6	LaMg _{0.05} Cr _{0.95} O ₃	K ₂ SO ₄	1373	1.6	315	1014
32	LaMg _{0.05} Cr _{0.95} O ₃	K ₂ SO ₄	1373	1.6	652	-
29	LaMg _{0.05} Cr _{0.95} O ₃	K ₂ SO ₄	1373	1.0	-	289
				3.0	-	1094
136	LaMg _{0.05} Cr _{0.95} O ₃	Illinois #6 + 10 mole% K ₂ O	1723	1.0	30*	67*
137	LaMg _{0.05} Cr _{0.95} O ₂	Montana Rosebud + 10 mole% K ₂ O	1723	1.0	164	<30

* Short run time; greater error in measurement.

TABLE 10. Electrochemical Testing of Rare Earth Doped Hafnia

Test	Compound	Electrolyte	Temp., °K	Current Density, A/cm ²	Corrosion, g/Coulomb	
					Cathode	Anode
91	0.1 Tb ₄ O ₇ -0.9HfO ₂	K ₂ SO ₄	1473	1.6	<5	<5
99	0.1 Tb ₄ O ₇ -0.9HfO ₂	Montana Rosebud + 10 mole% K ₂ O	1723	1.6	3	5
98	0.05 PrO ₂ -0.05Yb ₂ O ₃ - 0.05 Tb ₄ O ₇ -0.85 HfO ₂	Montana Rosebud + 10 mole% K ₂ O	1723	0.8	<10	<6

compositions have been fabricated. Three electrochemical tests conducted on two rare earth hafnates are listed in Table 10. These rare earth hafnates are the most resistant to attack both by the molten seed and Montana Rosebud slag of all the ceramic materials so far tested at BNWL.^(12,13) The attack is generally intergranular on the cathode. The grains seem quite chemically resistant to the slag/seed resulting in large grains being removed from the cathode-slag interface. The anodes generally have some chemical interaction with the slag along with the eroding of the grains due to bubble generation. SEM-EDAX analysis will be conducted on selected samples to better determine the corrosion mechanism. The role of rare earths on the electrochemical tests need to be determined. Preliminary post-test examination indicated a preferential leaching of the rare earth components by the potassium in the coal slag.

4.0 WORK ANTICIPATED DURING NEXT QUARTER

4.1 ELECTROCHEMICAL TESTING AND EVALUATION

The testing and evaluation of seed/slag in a dc electric field on potential MHD electrodes and insulators will continue. The work will emphasize the HfO_2 and YCrO_3 -base electrodes in coal/slag electrolytes.

4.2 ELECTRODE-INSULATOR DEVELOPMENT

The evaluation of yttrium chromite-base electrode materials will be completed. Fabrication of HfO_2 -doped with rare earth and other oxides will be emphasized using a precipitation technique.

4.3 CHARACTERIZATION AND EVALUATION

The characterization and evaluation of the electrodes, insulators, and current leadouts for the Phase III test of the US channel module in the USSR U-02 generator will receive priority attention. The major portion of the work will be completed during this quarter.

The evaluation of the thermal properties for the electrodes and insulator materials used in the Phase II U-02 test will be completed. This will emphasize the apparent thermal conductivity differences between like electrode materials, i.e., $\text{La(Mg)CrO}_3 \cdot \text{ZrO}_2$ composites.

The electrical conductivity measurements of HfO_2 and YCrO_3 base electrode materials will be initiated.

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