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Evaluation of Candidate Magnetohydrodynamic Materials for the U-02 Phase III Test

**D. D. Marchant
J. L. Bates**

June 1978

**Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PNL-2738

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EVALUATION OF CANDIDATE MAGNETOHYDRODYNAMIC
MATERIALS FOR THE U-02 PHASE III TEST

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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

As part of a cooperative U.S.-U.S.S.R program, this report evaluates electrode and insulator materials tested at the Westinghouse Electrode Systems Test Facility in Pittsburgh, Pennsylvania. From this evaluation materials will be selected for use in the third phase of tests being conducted in the U-02 magnetohydrodynamics test facility in the Soviet Union. Electrode and insulator materials were examined with both an optical microscope and a scanning electron microscope. The cathodes were found to behave differently from the anodes; most notably, the cathodes showed greater potassium interaction. The lanthanum chromite-based electrodes (excluding those fabricated by plasma-spraying) are recommended for testing in the U-02 Phase III test. Hot-pressed, fused-grained MgO and sintered MgAl_2O_4 are recommended as insulator materials. The electrode attachment techniques used in the Westinghouse Tests were inadequate and need to be modified for the U-02 test.

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INTRODUCTION

As part of the U.S.-U.S.S.R. open-cycle cooperative program, the United States has an opportunity to conduct tests in the U-02 magnetohydrodynamics (MHD) test facility in Moscow. Two tests, Phases I and II, have already been conducted in the Soviet Union. In preparation for the Phase III test, three screening tests, designated proof tests 1, 2 and 3, were conducted on electrode-insulator materials at the Westinghouse Electrode Systems Test Facility, Westinghouse Research and Development Center, in Pittsburgh, Pennsylvania.

Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute for the U.S. Department of Energy (DOE), evaluated and characterized the materials tested in the three proof tests. This report summarizes PNL activities and findings associated with this effort. The information developed through these proof tests and evaluations will be used to select the materials and designs for the Phase III test in the Soviet U-02 MHD test facility.

CONCLUSIONS AND RECOMMENDATIONS

In general, chromite (LaCrO_3 -) -based electrodes were less damaged by the test environment than were the spinels (Fe_3O_4 - MgAl_2O_4) or the hafnia-based electrodes. Potassium migrated into the spinels much more easily than into the chromites or hafnias. Potassium penetration, concentration, and interaction were more severe on both the cathodes and cathode insulators than on respective anodes and anode insulators. The spinels suffered severe potassium attack damage in the mid-temperature areas of the electrode interior. Potassium attack of the insulators was most severe on sintered Al_2O_3 and sintered, fine-grained MgO . Hot-pressed MgO and sintered MgAl_2O_4 showed much less potassium interaction.

In both the electrodes and insulators, potassium migrated along grain boundaries, open porosity, and cracks. Potassium then interacted initially with the impurities along the boundaries, resulting in enlarged grain boundaries, weaker intergrain bonding, and a disruption of the mechanical integrity of the compact. The sintered MgO was not well bonded and, because it was fine grained, had a large surface area. Increasing the grain size and the intergrain bonding (i.e., removing the porosity) decreased the reactivity of the fine-grained MgO .

In general, the electrodes were not fabricated with microstructural features that would minimize potassium penetration. Such microstructural features include no interconnected porosity of cracks and low impurity levels at the grain boundaries. The electrodes sprayed with plasma had the least favorable microstructural features. Both the hot-pressed and sintered electrodes had more favorable microstructural features, including less interconnected porosity, better control of impurities, and less cracking, than the plasma-sprayed materials.

The plasma-sprayed chromite had more impurities at the grain boundaries than the sintered or hot-pressed chromite. The major impurity was La_2O_3 , which hydrates readily and can disrupt the lattice. The plasma-sprayed chromites also had a tendency to delaminate. This delamination was partially due

to the hydration of La_2O_3 and potassium at the grain boundaries as lamination formed during fabrication.

All of the electrode attachment techniques had weaknesses and may not be adequate for channel designs where the electrodes are not held in place by sidewall overlap. Poor attachment affected both the thermal and electrical performance of the electrodes.

The electrode-insulator interactions occurred at the hotter temperatures at which the electrodes changed microstructurally (probably $>1400^\circ\text{K}$). In general the electrode materials migrated into the insulators. The migration occurred in the hotter areas of the insulator and resulted in an insulator microstructure comprising a mixture of electrode and insulator materials.

Testing different combinations of electrodes and insulators in the same channel resulted in some cross-contamination. Disregarding overflow from excessive heating (most overflow occurred with the spinel electrodes), the chromites caused the most contamination. Lanthanum or chromium contamination was found in all downstream electrodes both on the plasma surfaces and inside the electrodes along cracks and grain boundaries. Another major contaminant was the calcium-stabilized zirconia from the upstream combustor and nozzle assembly. The zirconia contamination was most severe in the first proof test. This contamination was mostly found near the plasma surface. The effects of both the chromite and zirconia contamination on the electrode-insulator performance could not be determined from these tests.

Two experimental phenomena must be considered when evaluating electrode performance: 1) electrical shorting between anodes and cathodes because of the development of conducting paths in the insulator sidewalls, and 2) electrical shorting through thermocouples placed in the electrodes. Both of these phenomena reduce the electrochemical effects in the electrodes and lead to overestimation of endurance capabilities.

Even though all electrodes and insulators had limitations in their performance, the chromite-based electrodes (excluding those fabricated by plasma-spraying or those containing SrZrO_3) are recommended for testing in the U-02 Phase III test. The recommended insulators are those made of hot-pressed, fused-grained MgO and sintered MgAl_2O_4 .

TEST PROCEDURES AND RESULTS

The Westinghouse Electrode Systems Test Facility comprises a combustor, a nozzle, a test channel, and downstream components. Toluene is used for fuel; the oxidizer is oxygen-enriched preheated air; the seed is K_2CO_3 in a water solution. The plasma has a temperature of about $2600^{\circ}K$ and a linear flow rate of about 450 m/sec in the channel. The heat fluxes in the electrodes are generally from 20-60 W/cm^2 . The current density established by using exterior power supplies generally ranges from 0.9 to 1.5 A/cm^2 .

For the proof tests evaluated here, the test channel consisted of a wall of 12 anodes and a wall of 12 cathodes separated from each other by two insulating sidewalls. The electrodes were positioned with a pitch of 1.36 cm. Each electrode was about 1 cm x 1.7 cm x 6 cm with a surface of 5 cm x 1 cm exposed to the hot plasma. The electrodes were individually mounted on copper cooling blocks. The cooling blocks were electrically insulated from each other by polyimide tape. Separate power supplies were used for each electrode pair.

The electrical environment during the test, together with other electrical measurements, will be summarized by Westinghouse. Heat fluxes through the electrodes will also be summarized by Westinghouse. This report emphasizes the examination of the microstructures of polished surfaces as observed with both an optical microscope and a scanning electron microscope.

In characterizing and evaluating materials from the proof tests, PNL examined both pretest and posttest samples. Instances where pretest samples were not available have been noted in the text. In general, the posttest samples were mounted by Westinghouse in Maraset,^(a) a ceramographic mounting medium. The samples were then sectioned into appropriate examination sizes either by Westinghouse, by the National Bureau of Standards (NBS), or by PNL. All final cutting, ceramographic polishing, and ceramographic examination were conducted by PNL. The specific cutting and mounting details for individual proof tests are outlined in the discussion of each test.

(a) Maraset is a mixture of Maragla's Hardener No. 555 and Maraset Resin No. 655 from Acme Chemicals and Insulation Co., New Haven, CT.

For the purpose of this evaluation, the electrodes have been numbered using a 3-digit numbering system. The first digit indicates whether the electrode is an anode (2) or a cathode (1). The last two digits indicate the electrode's relative position in the channel; the position nearest the channel inlet is 01 and the position at the channel exit is 12. For example, the cathode and anode nearest the channel inlet are numbered 101 and 201, respectively.

PROOF TEST NO. 1

The first proof test for the evaluation of Phase III U-02 candidate materials was conducted at Westinghouse on October 10 and 11, 1977. The test involved seven steps: 1) initial heatup, 2) establishment of operating conditions, 3) operation at steady-state, 4) measurement of electrical properties, 5) operation at steady-state, 6) measurement of electrical properties, and 7) cooldown. The electrodes and insulators were exposed to the hot, seeded plasma for 21 hr. Some of the electrodes were exposed to current densities of up to 1.25 A/cm^2 . Table 1 lists and characterizes the eight different electrode-insulator combinations tested in the first proof test. These combinations include differences in leadout compositions or attachment techniques. These eight electrode-insulator combinations represent five different electrode material compositions. Three insulator compositions were tested: MgAl_2O_4 , MgO , and Al_2O_3 .

After testing, the electrode-insulator channel was disassembled and visually examined. The anode and cathode walls were separately encapsulated in Maraset. Westinghouse cut the anode wall in half using a diamond saw with water cooling. The cathode wall was sent to NBS for cutting. Half of the anode and cathode walls were then sent to PNL for examination.

The portion of the anode wall that we received was severely cracked. To determine the amount of cracking from the initial diamond cut and to expose an area of the anode that was not washed with water (washing will remove water-soluble potassium compound), the anode was cut 0.95 cm (0.38 in.) from the center and parallel to the cut that had been made by Westinghouse. A SiC cutting wheel with kerosene coolant was used. To reduce the amount of

TABLE 1. Electrodes and Insulators for Proof Test No. 1

Electrode Insulator Combination	Channel Location	Material	Source	Fabricator	Fabrication Technique	Density, g/cm ³ (% TD)	Porosity			Attachment Method
							% Total	% Closed	% Open	
1 Electrode	101, 201	La _{0.95} Mg _{0.05} CrO ₃	General Refractory	Westinghouse	Hot-pressed at 1895°K and 1.38x10 ⁶ Pa	6.38 (96%)	3.94	3.93	0.01	Mechanical with silicone pad
Insulator		MgO	Norton	Norton	Fused-grain	3.01 (84%)	16.0	3.8	12.2	
2 Electrode	111, 211	La _{0.95} Mg _{0.05} CrO ₃	General Refractory	Westinghouse	Hot-pressed at 1892°K and 1137x10 ⁶ Pa	6.38 (96%)	3.94	3.93	0.01	Silver-filled epoxy to copper
Insulator		MgO, Al ₂ O ₃	Trans Tech	Westinghouse	Hot-pressed for 3 hr at 2.76 x 10 ⁷ Pa and 1873°K	3.13 (87%)	12.6	0.44	12.5	
3 Electrode	112, 212	La _{0.95} Mg _{0.05} CrO ₃	Cerac	Westinghouse	Hot-pressed at 1893°K and 1.37x10 ⁶ Pa	6.33 (95%)	4.62	4.14	0.48	Brazed to monel mesh
Insulator		MgAl ₂ O ₄	Trans Tech	Westinghouse	Hot-pressed at 1973°K and 4.14x10 ⁷ Pa	3.54 (98%)	1.45	0.77	0.68	
4 Electrode	102-104 and 202-204	Fe ₃ O ₄ -MgAl ₂ O ₄		General Electric	Sintered					Flexbed soldered to copper
Insulator			General Electric	Sintered						

TABLE 1. (contd)

Electrode Insulator Combination	Channel Location	Material	Source	Fabricator	Fabrication Technique	Density, g/cm ³ (% TD)	Porosity			Attachment Method
							% Total	% Closed	% Open	
5 Electrode	105-107	0.25Fe ₃ O ₄ -0.75MgAl ₂ O ₄	Trans Tech	APS	Plasma- sprayed to Hoskins 875					Hoskins 875 mesh brazed to copper
Insulator		MgAl ₂ O ₄	Trans Tech	Trans Tech	Sintered	3.46 (96%)	3.62	3.06	0.56	
6 Electrode	205-207	0.25Fe ₃ O ₄ -0.75MgAl ₂ O ₄	Trans Tech	Technectics	Plasma- sprayed to Hoskins 875	3.86 (96%)	4.21	4.17	0.04	Hoskins 875 mesh brazed to copper
Insulator		MgAl ₂ O ₄	Trans Tech	Trans Tech	Sintered	3.46 (96%)	3.62	3.06	0.50	
7 Electrode	108, 109, 208, 210	0.097Y ₂ O ₃ -0.163CeO ₂ - 0.74 HfO ₂	Cerac-ANL	ANL	Hot-pressed					Nichrome ware brazed to copper
Insulator		MgAl ₂ O ₄	Trans Tech	APS	Plasma-sprayed					
8 Electrode	110, 209	0.18CeO ₂ -0.82 HfO ₂	Cerac	ANL	Hot-pressed					Hoskins 875 brazed to copper
Insulator		MgAl ₂ O ₄	Trans Tech	APS	Plasma-sprayed					

electrode-insulator damage, many saw blade passes were made across the sample; the depth of cut for each pass was about 0.003 cm (0.001 in.). The newly exposed surface contained significantly fewer cracks, indicating that the initial diamond cut caused cracking of the specimen. The cracking of the cathode appeared to be similar to that of the anode face as exposed by the PNL cut, so no additional cuts were made on the cathode.

After cutting, the surfaces of the anode and cathode walls were polished and examined. Figure 1 shows the polished surfaces.^(a) The cathode erosion was fairly uniform along this cross section of the channel. The most eroded cathodes were in locations 102-104 and 108-110. The anodes were not as uniformly eroded. Excessive erosion was found on anodes 208-210. This excessive erosion led to greater erosion of the adjacent upstream and downstream anodes. Anode 204 also showed excessive erosion in some places. The lack of erosion of the upstream insulator on anode 205 appeared to have reduced the erosion of anode 204.

After separating the individual electrodes and insulators, both the anodes and cathodes were remounted in Maraset. The samples were polished using diamond in an oil coolant, and were washed in CCl_4 to remove excess oil. The samples were not in contact with water during the cutting, polishing, and handling procedures. They were stored in a vacuum desiccator.

The polished, unetched surfaces were examined using both the optical microscope (OM) and scanning electron microscope (SEM). The polished surfaces of all the anodes and cathodes were examined with the OM. Selected anodes and cathodes were further investigated using the SEM. The SEM is equipped with energy-dispersive x-ray analysis (EDAX) capabilities. Qualitative EDAX analyses were conducted on selected areas to determine the major chemical constituents of the phases. Since quantitative analysis was not conducted, the EDAX results can only be expressed as relative amounts of the various elemental species. To simplify the reporting of the SEM-EDAX results, elemental species in each compound will be expressed as elements, although the elements exist as oxides. If an elemental species is other than an oxide, such as a sulfide or metal, it will be identified as such.

(a) All figures in this report appear at the end of the text.

Electrode-Insulator Combinations No. 1-3

The Westinghouse LaCrO_3 electrode-insulator combination contains 5 mole% MgO . The fabrication parameters are found in Table 1. The microstructure of an untested $\text{La}(\text{MgCr})\text{O}_3$ electrode consisted of about $10\text{ }\mu\text{m}$ (somewhat equiaxed) matrix grains; a second phase in the shape of small, irregular grains; and a porous area along the grain boundaries about half the size of the matrix phase. The matrix comprised LaCrO_3 with about 2 mole% Mg . (With the EDAX, the detection limit is about 2 mole%.) The matrix also contained aluminum, silicon and potassium as impurities. The second phase (generally resolved at magnifications greater than 500X) was high in chromium and contained the remainder of the 5 mole% MgO . The second phase occupied about 5% of the area. The porous area was granular shaped.

For this test the LaCrO_3 electrodes were used as dummy electrodes in the upstream (101-201) and downstream (111-211, 112-212) locations in the channel. Consequently, they may not have been in the more uniform thermal environment that existed in the center of the channel. Three different techniques were used to attach the ceramics to the copper cooling block before the test:

- Electrodes 101 and 201 were mechanically attached to the copper cooling base using copper bars on the side of the electrode and attaching the copper bars to the cooling box copper by brass screws. The copper bars were squeezed lightly against the sample to hold it in place. A nickel-filled silicon pad was used between the electrode and the cooling copper.
- Electrodes 111 and 211 were attached to the copper using a silver-filled epoxy adhesive.
- Electrodes 112 and 212 were brazed to a Monel mesh. The Monel mesh was soldered to the copper cooling block.

In general, posttest examination of the electrodes showed that none of the attachment techniques was adequate. The mechanical attachments did not hold the electrodes against the cooling block. The silver epoxy did not maintain an attachment with the copper. Cracks developed in the ceramic in the areas where the Monel pad had brazed to the ceramic. More detailed

descriptions of the attachment problems will be given in the discussions concerning the individual electrodes.

The overall color of the anodes differed from the cathodes. The anodes had an orange-red hue on a darker, blackish background. The cathode generally looked more greenish brown. The greenish colors were associated with a reduced oxidation state. The fully oxidized lanthanum chloride was black. The cathodes degraded more than the anodes. Potassium penetrated the cathodes to a greater extent than the anodes. The cathode insulators also showed a greater attack by potassium than did the anode insulators.

Anodes for Combinations No.1-3. All three electrodes had massive microstructural changes near the plasma surface. The microstructural changes included grain growth, a coarsening of the porosity, and severe cracking somewhat parallel with the electrode base. Some of the cracks may have developed during cooldown, indicating a reduction in mechanical integrity if the electrodes are exposed to thermal cycle operating conditions.

Anode 201. Anode 201 is shown in Figure 2. As with all the photographs in this report, various portions of the figure are designated with letters and will be referred to in the paragraphs that follow. The average height of anode 201 is 1.93 cm, compared to its initial height of 2.08 cm, giving a loss of only 0.15 cm. The erosion resistance of the inlet nozzle adjacent to the electrode helped to reduce anode erosion. A major crack (A) was found in anode 201 about 1 cm above the base (B). It is evident from reactions found along the interface exposed by the crack that part of this crack had developed sometime during operation. A reaction zone was observed along the edges of the anode to the depth of the large cracks. Some of the reaction was with the metal-filled epoxy between the electrode and the insulator. The remainder of the reaction was due to seed attack. Below the large cracks no interaction was observed between the electrode, seed, or insulators.

Between the base of the electrode and a little below C, Figure 2 shows that the microstructure remained unchanged from the untested microstructures. Potassium was not found in this area except along the large crack at the center of the ceramic. At C, the second phase began to increase in chromium content. At F, the matrix LaCrO_3 is not chrome-depleted. The second phase

cannot be found at 3000X. The porosity has increased and may be due to the loss of the second phase. The grain boundaries are filled with calcium and silicon.

At E in Figure 2, the microstructure comprises three phases: 1) a LaCrO_3 phase with no chromium depletion (40% of area), 2) a lanthanum oxide phase with some silicon and calcium (55% of area), and 3) a LaCrO_3 phase depleted in chromium but concentrated in magnesium (about 5% of area). At F, the chromium-depleted LaCrO_3 is not found. The other two phases are found with the LaCrO_3 dominating (60% of the area). At G, there are two phases: 1) LaCrO_3 with no chromium depletion and 2) lanthanum oxides with some silicon and calcium but with no chromium or potassium (30% of area). The lanthanum oxide phase is located along grain boundaries of the LaCrO_3 . This phase may be the residue of the dissolution of the LaCrO_3 grain attributed to potassium attack. The potassium-chromium compounds may have migrated to the electrode-plasma interface (EPI) and vaporized, leaving a lanthanum-rich phase along the grain boundary.

At H, the area is porous with enlarged grain boundaries. The grains are single-phased and contain no potassium. In this area no chromium depletion was found even at the EPI. Hydration of the lanthanum at the grain boundaries would lead to the apparent enlarged grain boundaries and increased porosity.

At I, the protrusion is single-phased, mostly containing lanthanum oxide with a small amount of zirconium. The zirconia is from the upstream component and contains calcium. Although the calcium content of this zirconia is not constant, all of the zirconia-calcium composition will generally be referred to as calcium-stabilized zirconia (CSZ). All the compositions labeled CSZ originate in the upstream components. It does appear that the lanthanum-rich layer commonly found at the EPI has been swept downstream over the adjacent insulator; consequently, the lanthanum-rich layer is not found at H. Upstream from I at J, the EPI is chromium depleted. This area represents the type of surface generated from long-time exposure to the plasma. Below J at K, a small amount of chromium depletion is found in the LaCrO_3 . The second phase in this area is chemically different than the untested second phase because of the removal of chromium. In this second phase the MgO is the major constituent with smaller amounts of Cr_2O_3 .

The electrode and the MgO insulators interacted near the hot electrode surface in the restructured zone. The interaction and attachment of the electrode to the insulator caused cracks from the electrode to propagate through the adjacent insulators. In the recessed region some of the electrode material flowed across the insulator to the downstream anode (anode 202).

The downstream insulator is shown in Figure 2. The initial, single-phased MgO had some isolated areas of second-phase formation. At the plasma surface (L), the insulator had two granular-shaped oxide phases: 1) a lanthanum and zirconium phase (major phase) and 2) a magnesium phase with some potassium and a trace of iron. Figure 2 shows that the same two phases exist at M, except that the MgO phase does not contain iron or potassium. At N, the two granular-shaped phases are: 1) a MgO phase and 2) a ZrO_2 phase containing potassium and some calcium, lanthanum, and chromium. The ZrO_2 originated in the upstream components. At O, which was in a cooler area of the insulator near the electrode, the phases are: 1) MgO with no potassium or iron and 2) potassium and chromium with a small amount of magnesium. The components of this second phase migrated into the insulator along grain boundaries and pores. The second phase was found as far as 3 μm from the insulator-electrode interface. This second phase interacted with the insulator grains.

A metal-filled epoxy was found on part of the MgO insulator. The metal in the epoxy had partially oxidized in the area above O. In the oxidized regions, metallic silver was found in the form of islands surrounded by an oxidized alloy of nickel and copper, with some chromium. Little penetration of either the silver or the nickel-copper alloy was found in the insulator. Some copper was found in the electrode. The copper was only located in the electrode in the areas adjacent to the locations where the oxidized alloy was found.

The silver metal in the epoxy at the base of the insulator was not oxidized. The insulator separated from the copper. Although the epoxy adhered to the MgO insulator, it did not adhere to the copper. No silver-filled epoxy was found attached to the copper in the region where the insulator had separated from the copper.

The mechanical attachment did not hold the electrode tightly against the nickel-filled silicone pad. Some potassium penetrated along the crack between the electrode and insulator and was deposited by the pad. The copper on the side of the electrode was not in contact with the ceramic. As the electrodes heated during operation, the gap between the copper and the electrode decreased because of thermal expansion; the decrease, however, was not sufficient to close the gap. Consequently, in this test the electrode was not in good thermal contact with the copper and the heat transfer between the copper and electrode was restricted.

Anode 211. Anode 211 is shown in Figure 3. During the test, this anode eroded to an average height of 1.17 cm, compared to an original height of 1.68 cm; the loss in height was 0.51 cm. The erosion of anode 211 appeared to be affected by the excess erosion of the adjacent electrodes upstream. The effect on anode 211 of the excessive erosion of the adjacent upstream electrodes can best be seen by the erosion profile shown in Figure 1. A valley occurred with anodes 208, 209, and 210. The upstream edge of 211 was highly eroded because of this valley.

Anode 211 also contained a restructured region, with the corresponding grain growth, coarsening of the porosity, and second phase; its restructured region did not, however, have microstructural changes as massive as those in anodes 201 and 212. Between C and B in Figure 3, the electrode microstructure is similar to the untested microstructure. The two-phased region begins almost abruptly at B. About 20% of the second phase, which contains mostly chromium and magnesium, is found in this area. The second phase continues to coarsen between B and A. Around A, the second phase is in its greatest concentration, covering between 40% and 50% of the surface. Calcium-stabilized zirconia (CSZ) is also found in the area of A, but only in small amounts (around 5%); it is not found between A and the electrode-plasma interface. The surface consists mostly of the matrix phase, with a little second phase at the grain boundaries.

No La_2O_3 phase was found at the EPI. The La_2O_3 -rich phases that generally form after long-term, high-temperature exposure to the plasma might have eroded away near the end of the test after the upstream electrodes had

eroded excessively. The EPI examined in Figure 3 may have only existed for the last hour or so of the test.

An examination of the microstructure from C to A in Figure 3 indicates a change in porosity between those two points; the porosity is unchanged between C and B. At B, the porosity begins to coarsen; apparently the smaller pores decrease in size and the larger pores coarsen. At the EPI, the porosity is considerably larger than in the untested microstructure. Between these large pores, areas exist that do not have observable porosity (500X magnification). At the surfaces the pores are large and intermixed between large areas of dense materials.

The major grain growth of the matrix occurred near the EPI. This grain growth may be misleading since the second phase appeared to grow by the alteration of the matrix grains. No major grain growth was observed in the area where porosity decreased because of the coarsening process. Apparently, the grain boundaries still have impurities, a second phase, or small porosity to inhibit the grain growth.

Not as many dense, large grains were seen on anode 211 as on anodes 201 or 212. The excessive erosion may have eliminated most of the hotter restructured portions of the electrode. The dense particles at D are similar to the dense particles on the surfaces of anodes 201 and 202, and may represent material flowing from the surface as the test was completed. Material flow does not necessarily imply a molten state. Molten chromite is probably very fluid in the centipoise range. The fluidity may result in the immediate sweeping away of the material by the plasma. The flowing material may only be unmelted ceramic in the plastic state responding to the axial stresses caused by the plasma.

The restructured region began at 0.65 cm above the base as compared to 1.5 cm on anode 201. Anode 211 apparently ran hotter than either anodes 201 or 212. The separation of the anode from the copper cooling block could have caused the increase in its overall operating temperature. The silver-filled epoxy used to attach the electrode to the copper block remained attached to the electrode but separated from the copper. Some epoxy was found surrounding

the silver particles; therefore, the back surface probably did not exceed 573°K.

In general, little potassium was found in the electrode; the potassium found was between B and A. Some potassium attack was seen in the upstream surface at E.

Anode 211 reacted with both the MgO and spinel insulators. These reactions only occurred in the hotter restructured regions of the electrode. H. K. Bowen at Massachusetts Institute of Technology has found that reactions between chromite and spinel begin at about 1673°K. No reaction was predicted to occur between chromite and magnesia until temperatures reached 2273°K. It should be noted that these tests were not conducted in the presence of potassium, which might lead to lower-temperature reactions by forming intermediary compounds, or in an electric field where electron chemical interactions might lower the interaction temperature.

An axial crack from the adjacent upstream electrode went through the upstream insulator and into anode 211. The crack probably occurred during cooldown. The perpetuation of the crack through the insulator was evidence of attachment of the insulator to the electrode.

Anode 212. The erosion of anode 212, shown in Figure 4, was also affected by upstream electrodes and the downstream outlet section. Erosion of anode 212 led to erosion of the downstream exit chamber. The average height of anode 212 was 1.66 cm, compared to 1.93 cm originally, giving a loss of 0.27 cm. The restructured region began at 1.1 cm above the base of the ceramic, indicating that the ceramic ran cooler than the anode. The restructured region contained larger grains and porosity; but the large, dense areas on the surface, separated by porosity as found in anode 201, were not found in anode 212. The cracking in this anode was not as severe as in anodes 201 or 211.

Figure 4 shows that the microstructure at B consisted of two phases: 1) LaCrO_3 and 2) chromium and magnesium oxide. The third phase that was found near the surface in anodes 201 and 211, CSZ, was not found in anode 212. An area of high concentration of the second phase, as found in anode 211, was not found in anode 212. The maximum amount of second phase (A) is from 10%-20%.

The areas around D and E in Figure 4 consist of large areas of dense grains of matrix with small amounts of second phase. Large pores are found intermixed with the large grains. The surface near the center region of the electrode does not have the large grains.

During the test the electrode separated from the Monel mesh at the base. The separation occurred by the braze separating from the ceramic. The separation of the braze from the ceramic was clean, indicating a poor bond. Some potassium had penetrated the metal mesh area. Metal was found in the ceramic near the ceramic-braze interface and in isolated areas with the electrode to a depth of 0.2 cm from the ceramic base. This metal was probably braze that had penetrated the ceramic along the open porosity. This metal was not found in anodes 201 or 211.

The electrode reacted with the spinel insulator. The resulting bond caused the breaking of the insulator as shown in Figure 4. The reactions were limited to the restructured regions of the electrode.

Cathodes for Combinations No. 1-3.

For electrode-insulator combination No. 1, the cathodes degraded more than the anodes. More potassium was found with the cathodes than the anodes. More massive potassium attack of the insulators was found with the cathodes than the anodes. The Westinghouse cathodes were of the same design as their respective anodes. As with the anodes, all three bonding mechanisms failed close to the ceramic-metal-copper interfaces.

Cathode 101. Cathode 101, shown in Figure 2, eroded to an average height of 1.85 cm, compared to 1.93 cm for the corresponding anode and an original height of 2.08 cm. Severe cracking occurred in the hot region of the electrode. The cracking began at the restructured zone. Laminar cracking was found in the hotter regions. The microstructure between P and Q near the base of the electrode was similar to the untested microstructure. It consisted of two phases: 1) LaCrO_3 (90% of area) and 2) a chromium-magnesium oxide phase with small amounts of lanthanum. At R, the microstructure was still two-phased, containing a LaCrO_3 phase with no chromium depletion and a phase rich in chromium oxide with some magnesium and lanthanum. This chromium oxide

second phase contained more chromium than the second phase located between P and Q. Some potassium was found along the grain boundaries of the LaCrO_3 . At S, the phases present were a LaCrO_3 phase and a magnesium, lanthanum and chromium phase with some potassium. This second phase contained less chromium than at R. At the electrode-insulator interface close to R, deposits consisting mostly of lanthanum were found. Some of these deposits had hydrated after polishing, causing protrusion above the polished surface. At T, three phases were found: 1) LaCrO_3 with some chromium depletion, 2) lanthanum oxide with some silicon and calcium, and 3) MgO with some lanthanum, chromium and potassium.

At the EPI, (U), three phases were present: 1) LaCrO_3 that was slightly depleted in chromium, 2) lanthanum oxide with some calcium, silicon, and a trace of chromium, and 3) MgO . The EPI at U was covered with a layer of MgO . Part of the upstream insulator had flowed onto the electrode. About half of the electrode was covered by the insulator. The microstructure of this MgO layer did not indicate a solidification from the melt. Hence, the MgO flow was caused by the plasma shear stresses while the electrode was mainly in the solid state.

Below the surface layer of MgO , a two-phased area was found with the matrix of LaCrO_3 without chromium depletion and CSZ at the grain boundaries. The CSZ contained some lanthanum.

Interactions occurred between the restructured areas of the electrode and the adjacent insulators. The interaction occurred only in the restructured region of the electrode. The interactions included penetration of the MgO by chromite and vice versa. Chromite penetration into the insulator occurred along the MgO grain boundaries. The MgO penetration into the electrodes was not as extensive and may also have been a grain boundary phenomena.

The electrode separated from the nickel-filled silicone pad; the mechanical attachment did not seem able to adequately hold the sample. Although the attachment was poor, in this test the electrode remained in contact with the channel wall because its outside transverse edges were held by the side insulator walls.

Microstructural changes occurred in the upstream insulator between W and the plasma surface; this insulator originally comprised single-phased MgO with a wide range of grain sizes and irregularly shaped porosity. At W, two phases were found: MgO and CSZ containing some iron. At X, the CSZ second phase did not contain iron. The insulator surface was coated with a layer of CSZ. The layer of CSZ had an oxide second phase at the grain boundaries that contained magnesium, silicon and a small amount of calcium.

Potassium leakage from the sample was found after polishing and placing the sample in a vacuum. This leakage indicated a high concentration of potassium. Potassium was found in the space between the electrode and the insulator. The potassium severely eroded the insulator beginning 0.67 cm from the base of the insulator. The potassium penetrated the MgO along the grain boundaries and interacted with the MgO, causing enlarged grain boundaries.

The upstream insulator separated from the copper block. The silver-filled epoxy used to attach the insulator separated cleanly from the copper. Potassium was found in this separated gap. This potassium interacted with the Maraset used to mount the sample for polishing.

The downstream insulator, also MgO, was of the same initial microstructure as the upstream electrode. The essentially single-phased MgO at Y in Figure 2 contained a trace of nickel. Occasionally an impurity phase containing potassium, silicon, and nickel was located along the grain boundary. At Z, islands of a magnesium-chromium oxide phase were found in the insulator close to the crack. Both potassium and chromium were found in the crack area. The potassium in the crack interacted with the electrode adjacent to the crack and formed a reaction zone of high porosity and chromium depletion. At AA, the grain boundaries contained potassium and chromium; at all other points the insulator was MgO. At BB, the second phase along some of the grain boundaries contained silicon, calcium and lanthanum, with small amounts of magnesium and potassium. At CC, three phase amounts were found: 1) MgO (90% of area), 2) LaCrO_3 (5% of area) and 3) CSZ containing lanthanum (5% of area). LaCrO_3 was no longer found near the plasma interface. Magnesium oxide was the major phase, and the second phase found on some of grain boundaries was CSZ that contained lanthanum. The insulator surface was also contaminated with chromium, iron and nickel.

Potassium attack was found in the mid-area of the downstream insulator. Although some of the potassium may have migrated along the crack between the electrode and insulator, the majority of the attack appeared to come from potassium penetrating from cathode 102 through the spinel insulator to the MgO.

The downstream insulator also separated from the copper cooling block. The silver epoxy remained on the MgO and separated from the copper. Potassium was not found in the gap between the insulator and the copper.

Cathode 111

Cathode 111 (Figure 3) eroded much more than anode 211. The shape of the erosion surface indicated the influence of a greatly eroded upstream electrode. The upstream edge eroded to the level of the upstream electrode; the downstream edge eroded to the general level of the downstream electrode.

A massive crack was found separating the restructured zone from the unrestructured zone. The crack continued through the downstream insulator into the downstream electrode.

The microstructure at F in Figure 3 appears unchanged from the untested microstructure. It has two phases: 1) a LaCrO_3 phase with trace quantities of silicon, aluminum and potassium and 2) chromium oxide with some lanthanum and magnesium. Generally, potassium is not located in the unrestructured areas below the large crack except along cracks and in some pores. At G, the two phases have the same general composition as F, except that the amount of the chromium-rich second phase has increased. At H, the LaCrO_3 is of the same composition as at F; the second phase has increased and contains more lanthanum. Figure 3 also shows that at I near the EPI the LaCrO_3 phase is slightly depleted in chromium. The second phase is mostly chromium oxide with little magnesium or lanthanum. The chromium grains are generally more than twice as large as the second phase at F. The chrome phase is about 30% of the area. At the EPI some thin growths of lanthanum are observed.

During testing, the electrode separated from the copper. The electrode was tilted in the direction of the plasma flow. This tilting could have

exposed the upstream insulator to the potassium-seeded plasma. Unlike the anode, little of the silver-filled epoxy remained on the ceramic, but adhered to the copper.

Electrical contact between the electrode and copper occurred in the corner of the electrode (around J and K) where the restructured region was located. High current densities in this area resulted in localized heating and consequent microstructural changes. In this restructured zone, large matrix grains were found with little porosity and second phase. It was a somewhat similar microstructure as the EPI.

The microstructural changes became apparent at the area marked J in Figure 3; the crack at J generally outlines the beginning of gross microstructural changes. The microstructure at this point comprises two phases: 1) LaCrO_3 with no chromium depletion (40% of area) and 2) chromium oxide consisting of some magnesium and aluminum. At K, the material is higher in porosity. The microstructure shows an intermixing of the phases such as those found upon solidification from a melt. The first phase contains lanthanum-rich LaCrO_3 (70% of area). The second phase is mostly chromium oxide with some magnesium and aluminum. The same two phases found at location K are also found in the insulator region at L. The insulator immediately next to the phase at L had no lanthanum or chromium penetration, indicating that the time at high temperatures was not sufficient to allow measurable lanthanum or chromium migration. The similarities of this microstructure with that of the surface indicate similar temperatures. The lack of interpenetration of the insulator and the restructured electrode area implies that excessive temperatures were not maintained for extended periods of time. Pieces of metal were found in the restructured region. These metal pieces were probably from the silver-filled epoxy. The electrode also interacted with the spinel insulator in the restructured region.

Cathode 111 also interacted with the downstream spinel insulator in the restructured region near the top of the electrode. The top surface of the downstream insulator was covered with electrode material that had flowed from cathode 111. The dense material at the top of this insulator was LaCrO_3 . A reaction interface was found between the LaCrO_3 and the spinel. Apparently,

the chromite penetrated the spinel; some spinel grains were also found in the chromite. The interaction of the electrode and insulator allowed the crack in the ceramic to perpetuate through the insulator.

The upstream insulator was made of alumina (Al_2O_3). Alumina insulators were not scheduled for operation in these clean fuel tests, since alumina interacts quite rapidly with potassium at temperatures above 1600°K . The insulator was partially exposed to the plasma because of the excessive erosion of cathode 110. The upstream insulator was also capped with a dense material. This dense material was not chromite, but was from the hafnia electrodes upstream. The surface layer was three-phased: 1) Al_2O_3 containing potassium and some iron, 2) elongated oxide grains containing aluminum, potassium, cerium and iron, and 3) an oxide grain boundary phase of hafnium, zirconium and a little cerium. Figure 3 at M shows that in the highly corroded zone the major phase contains aluminum and potassium with some cerium, chromium and lanthanum. The minor phase at the grain boundaries contains potassium.

Extensive potassium interaction was found throughout the insulator. This insulator showed the most extensive potassium interaction of all the insulators in the test. Potassium was found along the grain boundaries and was transforming the alumina grains (probably forming a type of β alumina).

Potassium also penetrated the spinel, but not as extensively as did the alumina. In the spinel, potassium was found at the hotter regions of the insulator near the chromite cap. The potassium penetrated from along the grain boundaries in the areas adjacent to the electrode to the areas near the electrode base. Potassium migrated along the gap between the electrode and insulator. The migration probably occurred earlier in the test, prior to tilting and electrode material flow.

Evidence of potassium was also found in various areas in the electrode. The cracks near the base of the electrode were outlined by areas filled with potassium. During metallographic preparation of the sample, potassium continually leaked from areas such as A in Figure 3. The increased potassium content of the upstream insulator may have led to the enhanced corrosion of the electrode-insulator interface.

Cathode 112.

Cathode 112, shown in Figure 4, had eroded more than its corresponding anode (anode 212). Most of the restructured area near the plasma surface was separated from the essentially nonrestructured area by a large crack (G). The exposed surfaces of the crack showed evidence of potassium attack, indicating that some type of crack existed during operation and did not develop solely on cooldown. The area between H and the large crack at G had a microstructure similar to the untested samples. Some restructuring occurred around I, showing a growth of the second phase as seen in mid-temperature areas in cathodes 101 and 111. The upstream area above the crack had microstructural development similar to the higher-temperature regions of cathodes 101 and 111. The amount of second phase increased to 40%-50% near the surfaces and then decreased in the large grains immediately at the surface. The depth of large grain area in this cathode in the upstream area was greater than in either cathodes 101 or 111.

The restructured area around J is unique to this electrode. The downstream electrode material had flowed over the adjacent downstream insulator. The insulator did not remain with the cathode wall when it was removed from the channel immediately after the test; consequently, it is not shown in the micrograph. The restructured region shown at K consists of four phases. The LaCrO_3 matrix dominates, representing generally 40% of the area. The second phase, a lanthanum-rich oxide, is about 20% of the area. This phase is irregularly shaped and is found on both grain boundaries and as isolated islands. A third phase, MgAl_2O_4 , is found around the crack. The fourth phase is metallic. The metallic phase is found along the crack and as particles throughout the area. The metallic precipitate is found only in this area of the sample. The source of the metal is unknown; it may have come from some coating used on the downstream insulator or channel exit area. Many small cracks are present in this area. The cracks seem to follow the grain boundaries. Some potassium is associated with grain boundaries and pores.

The EPI at L is in an area that had flowed over the insulator. The two phases in the overflow area are LaCrO_3 and magnesium-chromium oxide. The

intermixing of the two phases indicates that a melting and resolidification occurred.

The restructured region of the electrode also interacted with the upstream spinel electrodes. At the reaction interface, spinel grains were found in the chromite and chromite was found along some of the spinel grain boundaries. The interactions did not occur in the nonrestructured areas.

Little potassium penetrated the sample. Potassium was found in the restructured areas but generally not in the nonrestructured areas. A potassium reaction zone was found on the downstream side of the electrode in the nonrestructured zone at M. Potassium reacted with the grain boundaries around this area and immediately below M.

The electrode separated from the Monel pad. The separation left little braze metal at the ceramic surface. The only area in which metal remained with the ceramic was at H. No penetration of the metal into the ceramic or chemical interactions between the metal or ceramics were observed.

Electrode-Insulator Combination No. 4

The second electrode-insulator combination evaluated by PNL was fabricated by General Electric and comprised a magnesium aluminate ferrous ferrite ($\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$) electrode attached to a copper cooling block by means of an Inconel-600 flexbed.^(a) Grafoil was also used in the flexbed. The ferrite was single-phased at 300X magnification. The insulators were magnesium alumina spinel. Nickel strips were used to attach the insulators to the copper cooling block. A higher porosity was observed on a polished cross section because poor bonding of some of the grains caused small particles of the material to pull out during polishing.

The electrode was attached to the flexbed by means of metal filling three longitudinal grooves cut into the ceramic. Prior to filling with metal, no cracks were observed in the ceramic around the grooves. The metal-filled grooves are referred to in the report as "fingers."

(a) General Electric proprietary design.

Anodes for Combination No. 4. All the anodes and insulators eroded; the downstream electrodes showed the greatest wear. For the three anodes, the ceramic eroded from an initial height of 1.4 cm to an average height of: 1) 1.26 cm for anode 202, 2) 1.20 cm for anode 203, and 3) 0.84 cm for anode 204. The top surface of each of the anodes had an area of gross microstructural changes. The areas consisted of large, irregularly shaped pores and larger grains; some areas had deposits of potassium and a third phase. The gross restructuring indicates operating temperatures greater than 1800⁰K. Some of the anodes, especially anodes 203 and 204, flowed across the adjacent downstream insulator. Between anode 202 and 203, the insulator recessed about 3 mm below the level of the electrode and the electrode material filled the 3-mm recession area.

The anodes and the insulators reacted with one another. Some bonding occurred at the higher-temperature regions in the restructured zone. At lower temperatures iron was found in the insulators along cracks in the insulator.

The metal (Inconel-600) used to attach the insulators to the copper oxidized at the hotter temperature. This oxidation caused a volume change that, in some instances, may have produced stresses that caused the insulator to crack.

Cracks radiated from the tips of the three cuts made in the ceramic for the attachment to the flexbeds. The cracking in this area was quite extensive. In anode 202, part of the electrode began to separate from the flexbed because of the crack.

The bases of the anodes were not fully brazed to the flexbed. Many small separations were found between the metal and the ceramics. The major bonding of the anodes to the flexbed seemed to be due to the semimechanical holding of the fingers. The flexbed was firmly bonded to the copper. A reaction zone was found in the copper where the flexbed was attached. The solder joint next to the copper was quite porous. The porosity in this solder can greatly affect the heat transfer characteristics of the braze.

Small amounts of potassium were found in the carbon foil found in the flexbed. Potassium was also found in the cracks between the electrode and insulator and in pores in the restructured region.

Anode 202. Figure 5 shows anode 202. This anode was attached to the current leadout by metal fingers. Four phases were found around each of the fingers at A. The matrix was the dominant phase, representing at least 70% of the area. An iron oxide phase (10% of area) was found around some grain boundaries and in some porosity. The third phase, seen only at magnifications above 1000X, was iron-magnesia-spinel with manganese. Small amounts of manganese were also found in the matrix grains at the base of the anode. A fourth phase, which was small and granular, was metallic and contained molybdenum, calcium and iron. Molybdenum was occasionally found as a porous layer between the nickel-gold-copper braze and the electrode. The molybdenum was present as an alloy of molybdenum and manganese with small amounts of iron, nickel and copper. This alloy was probably used for the molybdenum-manganese pretreatment of the ceramic as part of the braze technique. The molybdenum from the prebraze treatment penetrated the ceramic, resulting in the formation of the small amount of fourth phase. No manganese was found in this phase. A greater concentration existed around the middle finger than the two side fingers.

The remainder of the microstructure of the ceramic up to C was similar to the untested sample except for cracking. A series of intergranular horizontal cracks was found at B. The vertical crack in the center of the sample was present before the test.

At C, a second phase began to form along the grain boundary. About 10% of the area was second phase. The amount of second phase was not constant between C and D. It decreased in the area around D, then increased again as the EPI was approached. This second phase was spinel that contained potassium.

A third phase can be seen at L in Figure 5. This phase, mainly found at the matrix grain boundaries, is composed mostly of lanthanum. The lanthanum is located all along the reaction zone. The lanthanum originated in the upstream electrode. It apparently migrated into the spinel to a temperature zone and deposited. The lanthanum deposits were not found at the hotter EPI area. A fourth phase can be seen at C but not at the EPI. This phase is located at the grain boundaries. The phase is mostly potassium with a small

amount of silica. The matrix grains at location E show a depletion of iron. The spinel at the EPI still contains iron but its concentration is less than E.

Potassium was found in the flexbed. Potassium leaked from both the top and bottom of the flexbed during metallographic preparation. The potassium was in the area where the grafoil was located. The large vertical crack between the middle finger and the surface was filled with potassium. Potassium migrated down the crack to the area of the middle finger. This crack was present prior to testing and acted as a path for gross potassium penetration. Other impurities, mostly manganese and silicon, were also found along the crack. Potassium also migrated between the metal strip and the downstream side of the electrode and into the cracks radiating from the metal fingers.

The nickel strip used between the insulator and the electrode oxidized at the higher temperatures. The volume expansion from oxidation is seen at F. The nickel oxide on the other side of the anode significantly expanded in size. The oxide layer was porous and contained potassium. Oxides of copper were found along with the nickel oxide in the area between the nickel metal and the insulator. Both molybdenum and potassium were found in the nickel oxide between the nickel metal and the electrodes.

Nickel oxidized at G. In the oxide layer were small islands of copper oxide. The nickel oxide also contained potassium. A reaction layer formed between the nickel metal and the insulator at G. The reaction layer was mostly nickel and potassium with some aluminum. The insulator immediately next to the reaction layer was spinel with some silicon, potassium and manganese inside the grains as impurities. No iron was found in the spinel in the locations where nickel separated the insulator from the anode. The oxide reaction layer between the nickel metal and the anode contained mostly nickel and potassium with some copper, manganese and iron.

Little reaction occurred between the spinel insulators and the nickel except where the nickel had oxidized. In the areas of nickel oxidation some nickel and copper were found in the anode to the depth of 500 μm . The insulator reacted with the anode in the restructured areas. As a result of the reaction, iron penetrated the insulator and grains of undoped magnesia-alumina spinel penetrated the electrode.

The tip of the upstream insulator was polyphased. The major phase, which covered about 50% of the area, was spinel. The granular second phase contained lanthanum and magnesium with a small amount of aluminum. A third phase, about 10% of area found along the grain boundaries, contained lanthanum and zirconium. Above the insulator was a two-phased mixture from the upstream electrode and insulator. This overflow material was mostly MgO at the areas closest to the plasma surface, and a lanthanum-zirconium compound beneath.

Anode 203. Anode 203 is shown in Figure 6. It has essentially the same general microstructural features as anode 202, except that it does not contain as much of the lanthanum-rich contamination phase in the area below the EPI. The restructured zone begins at A, a little below where the cracks were observed. The cracked region is extensive around A with a small intergranular crack formation. Some potassium may be associated with the cracking. Three phases are present between A and the large grains at the EPI. The large grains on the surface represent only the matrix and the chromium-rich second phase; none of the lanthanum-rich contamination phase is present.

The nickel metal at the side partially oxidized. A small amount of potassium was found in the oxide coating. Several areas of potassium concentration were found along the cracks separating the nickel from the anode. After metallographic polishing, potassium oozed out of the flexbed from B, which is in the grafoil part of the flexbed.

Pores constituted 30% of the braze joint between the flexbed and the copper. Since the major heat transfer from the flexbed to the copper was through this porous braze, thermal heat transfer characteristics of the electrode were affected by the porosity. The braze attached to both the Inconel and copper.

Anode 204. The restructured region for anode 204, pictured in Figure 7, can be seen above the crack at A. A small amount of second phase formed below the crack. The microstructure around the fingers was similar to that of anode 202. All three phases exist above the crack. The amount of zirconium lanthanum-rich phases was not as great as for anodes 202 and 203. Not as many dense grains were on the surface as with anodes 202 and 203. These grains eroded away during the test. The dense grains that remained were generally two-phased with the matrix grains the dominant phase.

Cathodes for Combination No. 4

The cathodes were more severely attacked by potassium and more eroded than the respective anodes. The cathode insulators were also more severely attacked by potassium than the anode insulators. The potassium attack resulted in large cracks in some of the interelectrode insulators. These potassium-filled cracks shorted the electrodes together as observed in the low interelectrode resistances found between electrodes (e.g., cathodes 102 and 103).

Cathode 102. Cathode 102 is shown in Figure 5. Dark areas, such as A, indicate an extensive region of potassium attack. The major potassium deposits were found inside the cathode and not at the hot electrode areas near the EPI. The dark band probably represents the temperature range where potassium salts were molten. Laboratory tests at PNL showed that molten potassium sulfate and carbonate are generally more reactive than either the gaseous or solid forms.

Of course, some potassium could have been removed from the surface by vaporization, since the samples were exposed to unseeded plasma for a period of time prior to cooldown. But even if the potassium were removed from the surfaces prior to cooldown, the effects of the potassium should still be seen in the surface regions with effects such as enlarged grain boundaries. These effects were not observed; consequently, it was felt that the most severe potassium concentrations were found in the center regions of the electrode even while under operating conditions. The potassium was driven into the sample by the electric fields and by the passage of current through the sample. Potassium was found around the center finger. Cracks from the center finger were filled with potassium. Potassium was found along grain boundaries on the areas at the tips of the fingers. These were the areas where electric current was being transported. Because of the high potassium content, the darker central region of the sample would not polish adequately to enable examination of the microstructure. Consequently, no phase identification could be made in this area. Potassium isolated grains of matrix. Apparently some of the grains dissolved in the potassium. Some potassium was also found in the gra-

foil near the ceramic interface. The grafoil also contained small amounts of zinc, nickel and iron.

The enhanced concentration of potassium at the cathode led to the severe potassium attack of the Inconel. At I in Figure 7, the potassium corroded the Inconel metal separating the insulator from the electrode and attacked the insulator. This excessive corrosion of the Inconel was not found at the anodes.

The excessive erosion of the nickel strip on the upstream insulator at J was also due to the presence of tin. Apparently, the flexbed was attached to the copper using a lead-tin solder that contained a small amount of zinc. Some of the solder must have remained on the nickel in the high-corrosion area close to the base of the cathode since tin was found throughout the high-corrosion area of the nickel. Tin forms compounds with the nickel that have low melting temperatures. The tin did not penetrate the insulator as did the potassium.

Partially because of the loss of the Inconel strip, potassium from the electrode penetrated the insulator. The vertical crack in the upstream insulator contained potassium. Potassium penetrated the insulator along the grain boundaries. The interaction of potassium with the spinel produced isolated grains of MgO . Apparently, Al_2O_3 was being removed from the spinel.

At K, a new phase appeared at the grain boundaries of the matrix. About 20% of the area was second phase. This second phase was found only between locations K and the EPI. The phase was mainly zirconium and lanthanum with minor amounts of iron, calcium, potassium and aluminum. The matrix in this area was of nominal composition with little depletion of iron. No other phases were observed in this area except occasionally a phase containing potassium. At M, the amount of lanthanum oxide precipitate increased to about 30% of the area. These precipitates contained less zirconium and more iron than those found at K. The matrix was somewhat depleted of iron. There were actually two lanthanum-rich phases in this area. They both had the same apparent reflectivity in the seam. The first phase was a lanthanum-rich iron-magnesium-aluminum spinel. The second was a lanthanum-zirconium oxide

compound. The two phases were intermixed and found side by side as bright phases penetrating the darker spinel matrix phase.

Five phases were found at L. The matrix phase had undergone some iron depletion. A fourth phase was also found at the grain boundaries but was mostly located between F and the surface where the grains had grown. This phase was an oxide containing magnesium and zirconium with aluminum and small amounts of iron. The fifth phase, found as occasional isolated grains, was an oxide of magnesium and iron with a small amount of nickel.

The EPI comprised areas of large grains of matrix with about 5% of the oxide phase containing zirconium and magnesium. This phase was at the grain boundaries. No lanthanum-rich phase was found in the surface region. The partially elliptical-shaped area above the top of the cathode was an artifact of the Maraset mounting medium.

The microstructure around the fingers at the base of cathode 102 was the same as found in anode 202 except that not as much of the iron phase was found in the ceramic. This iron phase contained some magnesium and aluminum. The manganese deposits found in the ceramic of the anode were not found in the cathode. Manganese, molybdenum and silicon were found as a second phase in the copper-gold-nickel alloys in the metal that filled the fingers in the cathode. However, this phase did not migrate to the sample.

The ceramic remained in contact with the flexbed, but severe cracking occurred, radiating from tips of the fingers. Differences in the coefficient of thermal expansion between the ceramic and the metal would lead to this type of cracking, since the stresses would concentrate near the tips. The unstructured areas of the electrodes were severely cracked. The electrode partially flowed over some of the downstream electrode.

Cathode 103

Cathode 103, pictured in Figure 6, eroded severely. The center regions of the sample showed high potassium concentration and interactions. The potassium concentration in either the hotter areas (near the EPI) or the colder areas (near the copper) was not as great as in the central area. Potassium reacted both with the Inconel between the electrodes and insulators and with the insulator in this mid-temperature region. Some potassium did

penetrate along the separation between the insulator and electrode to the area immediately above the thermocouple in the flexbed (C in Figure 6). The area around the end of the thermocouple contained potassium. Potassium was found in the castable material used with the placement of the thermocouple. There was no evidence of potassium interaction with the thermocouple wires.

The downstream insulator also eroded severely. In one area, electrode material flowed downstream across the insulator to cathode 104. The downstream insulator and the cathode interacted in the restructured region. Iron ions diffused into the insulator at these reaction interfaces.

In the area about 0.63 cm above the base of the ceramic the color of the cathode changed from black to a reddish brown, probably as a result of the formation of hematite (Fe_2O_3). The hematite formation implies a higher oxygen potential than the nonhematite formation area.

Cathode 104

Cathode 104, shown in Figure 7, also reacted severely with potassium. Potassium was found in the central regions. Potassium penetrated into the downstream insulator through holes in the Inconel-600 metal separators. Some potassium was also found in the top areas of the flexbed in the grafoil. A reddish color, attributable to hematite, was observed in the area of maximum potassium interaction.

The electrode was severely cracked. Cracks also radiated from the attachment fingers. Potassium migrated along the paths to the metal in the fingers. Some of the metal in the fingers seems to have reacted with potassium. Figure 7 shows that the grain boundaries at B were attacked by potassium.

The electrode surface generally consisted of the large matrix grains, along with about 20% of the lighter second phase. The lanthanum-rich third phase, found immediately below the highly restructured surface area, was not found at the surface. A light, iron-rich phase was found at the base of the electrode around the area of the fingers. The surface of the cathode also included areas of iron-depleted spinel; this spinel could have been part of the adjacent insulator or a spinel depleted of iron by vaporization.

Electrode-Insulator Combinations No. 5 and 6

The third electrode-insulator combination comprised anodes manufactured by the Technetics Division of Brunswick Corporation and cathodes manufactured by APS Materials, Inc. The anodes were made of 0.25 m/oFe₃O₄·0.75 m/oMgAl₂O₄ magnesium aluminum ferrous ferrite (MAFF) that was plasma-sprayed onto Hoskins 875 (72 w/oFe, 22 w/oCr, 5.5 w/oAl and 0.5 w/oSi) wire mesh. The wire mesh was then brazed to the copper cooling block. The cathodes were made by plasma-spraying MAFF-31 (Trans Tech Inc. 0.25Fe₃O₄·0.75 MgAl₂O₄) on a graded cermet. The cermet graded from a ceramic metal mixture near the ceramic to all metal near the wire mesh. The metal wire mesh was attached to the copper cooling channel. The cathode insulators were monolithic pieces of spinel that were attached to the cathodes at the copper blocks using silver-filled epoxy adhesive.

Anodes for Combinations No. 5 and 6. The initial microstructure of the anodes was not available for examination by PNL, but was said to be two-phased. The small amount of second phase was FeO. The porosity was somewhat lamellae, giving a layered appearance. Each of the posttest anodes reflected a loss of material. As shown in Figure 1, the metallographic surface of electrode 207 had enhanced erosion. This enhancement appeared to be connected with the erosion of the adjacent downstream anode, anode 208. The average heights of the anodes were 0.91 cm for anode 205, 1.01 cm for anode 206, and 0.65 cm for anode 207. The initial height of all three anodes was 1.37 cm. All of the anodes showed gross microstructural changes in the regions near the plasma. For all three, the electrode material flowed from one anode across the insulator to the downstream anode.

Gross examination of the fabricated anode blocks showed both transverse and longitudinal cracks segmenting the anode. The edges of the anodes were rounded.

Several cracks were seen in the anode surfaces when the anodes were visually examined immediately after removal from the channel. Many of their cracks were in the same general area as the cracks in the untested samples. The posttest cracks had grown through the adjacent insulators. The insulators were also severely cracked in the areas below the anodes.

Anode 205. Anode 205 is pictured in Figure 8. Immediately above the wire mesh (A), a single phase in a layered structure was present. At 250X magnification no second phase could be identified. Along with the layered ceramic structure were many cracks. These cracks were 20-50 μ m long and were parallel to the ceramic layers. A major separation was found between the restructured and unrestructured area B. Potassium deposited in this separated region. In the restructured area, between the crack and C, a third phase, MgAl_2O_4 , had formed. None of the original FeO second phase was found around the crack. The MgAl_2O_4 phase was found close to the crack and was dominant, covering over 50% of the area. Close to D, a new phase began to form and the amount of MgAl_2O_4 decreased. Above D, very little MgAl_2O_4 phase could be located; the new phase was about 30% of the area. At the EPI this new phase was about 5% of the area and mostly located at the grain boundaries of the large matrix grains.

The restructured area reacted with the MgAl_2O_4 insulator. Part of the MgAl_2O_4 in the anode was probably from the insulator. The bonding of the anode to the insulator may have helped keep the restructured anode portion above the large horizontal crack attached to the electrode. The upstream insulator darkened on the surface closest to the plasma. Iron oxide from either the upstream or downstream anode was the source of the color change. In the insulator region where the brownish color exists, the initial single-phase material was two-phased, with the second phase forming on the grain boundaries. This second phase at the surface was about 30% of the area.

The downstream insulator eroded to below the level of the anode and anode material flowed across the insulator to anode 206, as seen at E in Figure 8. Posttest visual examination revealed that a large amount of anode material had flowed in the area of the microscopic cross section. Other areas of anode 205 did not have this massive amount of material transfer. The anode material that flowed over the insulator at the interface between the anode and the insulator contained all three phases. Immediately above the interface between the anode material and the insulator, the relative amounts of phases were: 60% second phase, 5% third phase, and 35% matrix. The large grains at the surface contained only the second phase (30%) and matrix.

Potassium was found in the wire mesh. Potassium was not found in the unrestructured part of the anode.

Anode 206. The restructured region of anode 206, shown in Figure 8, did not separate from the unrestructured regions. The microstructure in anode 206 was similar to that of anode 205.

At the EPI, the grains were large and dense, and were generally separated by large pores. The EPI microstructure was single-phased and considerably depleted in iron. Two phases were found at F. These phases were: 1) CSZ with a little iron and 2) MAFF that was slightly depleted in iron. At G, which was at the interface between the region of gross microstructural changes and the essentially unrestructured region, three phases were found: 1) a granular CSZ phase and iron with a little magnesium and aluminum, 2) another granular phase containing potassium, aluminum and iron with a little magnesium (this phase was intermixed with the third phase), and 3) MAFF with potassium and a higher iron concentration than the untested matrix.

The microstructure at H showed four phases, which included the three phases described for G and a fourth phase containing lanthanum and zirconium. The only phase at I was a MAFF phase slightly depleted in iron. No potassium was found along the grain boundaries. At J, the anode material appeared single-phased at 300X with a little potassium both in the grain and at the grain boundaries. At 3000X thin bands of iron-depleted MAFF were found. At K a two-phased region was apparent above the metal wires. SEM examination could not find a phase that was different compositionally, but microstructurally it appeared to be poorly crystallized grains. A dense area was found at K that was single-phased and contained MAFF with some potassium along the grain boundaries. Part of the crack in the finger was filled with particles of lanthanum and iron that contained smaller grains of potassium, calcium and aluminum. The lanthanum probably came from electrodes 101 and 201. It was not known how detrimental the lanthanum may have been to the performance of anode 206. It is important to note the amount of contamination that can occur between dissimilar electrodes.

At L, which was a highly reactive zone, potassium was found along grain boundaries. The MAFF was depleted in iron.

The crack in the insulator filled with potassium. Next to the reaction zone the insulator itself was two-phased with islands of potassium and aluminum (containing small amounts of Mg) in a matrix of MgAl_2O_4 grains.

Anode 206 was severely cracked. The longitudinal cracks, which completely traversed the sample, showed evidence of potassium attack on the exposed surfaces, indicating the crack existed during at least part of the time the anode was at operating conditions. The other major horizontal crack also showed evidence of potassium interaction. The downstream insulator of anode 206 also eroded; the eroded surface was covered with electrode material. Examination of the anode surface immediately after the test showed that 30% of the downstream insulator was covered with electrode material.

Anode 207. Anode 207, also shown in Figure 8, exhibited the greatest amount of erosive wear. The shape of the wear on the micrograph indicated that the electrode was affected by the excessive erosion of the downstream electrode. Since this electrode had the greatest erosion, the metal-ceramic interface could have been hotter than for either anode 205 or 206. No interaction was observed between the Hoskins 875 and the ceramic. The Hoskins metal mesh did not oxidize. Microscopic observation showed the ceramic that had penetrated the metal to be reddish in color, indicating hematite formation.

The restructured area was separated from the unrestructured area by a crack in the restructured zone. All three phases existed in the surface area. On both anodes 205 and 206 the surface layers only had two phases. Apparently the surface layers flowed downstream, exposing the three-phased area of the sample just prior to cooldown. The downstream insulator was covered with electrode material. Examination of the surface prior to cutting for microscopic inspection showed about 60% of the downstream insulator was covered with electrode material. A portion of the downstream insulator was missing, as shown in Figure 8. The area appeared to have been subjected to chemical attack. Since this gross insulator attack was found on anodes 208 and 209 and not on the similar upstream anodes (anodes 205 and 206), it appeared that the enhanced erosion of the insulator was due to the excessive wear on potassium

concentrations in the downstream anode (anode 208). The excessive wear exposed the insulator to greater amounts of potassium.

The ceramic penetrated the wire mesh to a depth of about 0.08 cm. Anode 207 had an almost continuous series of horizontal cracks immediately above the metal. In this sample cracks also radiated from some of the metal mesh wires surrounded by the ceramic. Both of these cracking patterns indicate thermal stresses; however, there were cracks throughout the sample and the radiating cracking occurred in the area of maximum erosion, possibly because of higher temperatures and temperature gradients. Consequently, for the general design condition, the mesh ceramic bond maintained integrity. No reactions were found between the mesh and the ceramics. The metal had not oxidized.

As with anodes 205 and 206, the mesh on anode 207 was adequately bonded to the copper cooling block. No evidence of debonding was found between the wire and the copper. Some potassium migrated into the metal mesh area but did not appear to have reacted with the metal. The migration probably occurred along the openings between the electrode and insulator.

Cathodes for Combinations No. 5 and 6

Cathodes 105, 106 and 107 had more ceramic remaining than the corresponding anodes. A comparison cannot be made directly, since different vendors fabricated the respective electrodes. For each of the cathodes, the wire mesh remained attached to both the copper and the ceramics. No cracking was observed around the metal wires where the wires were attached to the metal leading to the cermet. Cracking was found in the ceramic around the interface between the cermet and the ceramic. The cracking is evidence of stresses, perhaps caused by thermal expansion mismatches. The mesh remained attached to the copper cooling block.

Potassium attack was not significant in the mesh-cermet area except in cathode 105 where potassium penetrated to the metal-cermet region, perhaps through the crack in the insulator, resulting in severe attack at the cermet.

Cathode 105. Figure 9 shows cathode 105, which is separated into two areas by a large crack. Microstructural changes occurred in both areas.

Since the microstructural change seen in this sample was similar to that of cathode 107, the SEM analysis was only conducted on anode 107. The figure shows that the ceramic is single-phased and quite porous close to the cermet. Some of the porosity may also be due to potassium interactions, since potassium is present throughout the ceramic material. The second phase begins to appear about midway between the cermet and the large crack. The second phase is at the grain boundaries. Above the crack toward the surface, the third phase is beginning to develop. The areas of maximum third-phase growth are not as concentrated in the third phase as in anodes 205, 206 or 207. Near the EPI a fourth phase is found. This fourth phase is found growing into the grains from the surface but not on the surface itself. The surface is mostly matrix, with less than 10% second phase.

The restructured region of the electrode reacted with the insulator. On cooldown some of the upstream electrode remained with the insulator, while some of the downstream insulator remained with the electrode.

Severe potassium attack occurred on the upstream insulator at the same level as the potassium attack in the cermet region. The potassium must have been molten in this region, indicating a temperature of at least 1223⁰K. The potassium-filled insulator crack may have been responsible for the low electrical resistance between cathodes 104 and 105. Potassium migrated between the electrode and insulator down as far as the metal mesh area. Potassium was also found along the grain boundaries in the area of the upstream insulators close to where electrode material had overflowed at A. Potassium was found throughout the electrode ceramic except at the hot surface areas.

Cathode 106. Cathode 106, pictured in Figure 9, was not as severely damaged as cathode 105. The difference was probably due to the effects of the platinum thermocouple and the castable. In this instance the castable may have acted as an electrical insulator and reduced the amount of current passed through the sample in this location; the thermocouple may have been a heat sink, resulting in a lower temperature of operation of this area of the cathode; the thermocouple may have been the current leadout, thereby allowing the current to bypass portions of the cathode.

Some potassium was found at the base of the cathode in the metal mesh. No reaction was seen between the potassium and the Hoskins metal. The mesh was quite porous and was filled with Maraset. Above the open mesh the nickel-plasma spray was found penetrating around the wires of the Hoskins mesh. No nickel was found in the mesh. The cermet was separated from the spinel by a crack. The structure of the cermet was of an interpenetrating stratified nature. The MAFF contained some nickel-molybdeum, magnesium or aluminum, and some iron was found in the nickel. A third phase, less than 2% of area, was found to contain iron and nickel. The MAFF above the crack did not contain nickel and was single-phased.

Other than some potassium at grain boundaries and in the cracks, the MAFF remained single-phased between B and C. A mottle structure occurred between C and the castable. The second phase was the MAFF with potassium. Close to the castable area the two phases were evenly distributed, occupying about 50% of the area each. No significant iron depletion was observed

Three phases were found at D. The matrix grain, MAFF, occupied about 75% of the area and showed some iron depletion. The amount of iron depletion was greater in the MAFF matrix grains as the EPI was approached. At E, the MAFF contained about 5 mole% Fe_3O_4 . At D, the second phase occupied about 20% of the area and contained only magnesium and iron. This phase was granular and intermixed with the matrix. The third phase, located only at the grain boundaries, contained zirconium with some calcium. It was probably calcium-stabilized zirconia from the upstream components.

At E, the MAFF was only 55% of the area. The magnesium-iron oxide second phase occupied 40% of the area and the CSZ phase was at the grain boundaries. Only two phases existed at the EPI: the iron-depleted MAFF and the CSZ phase containing potassium.

Potassium penetrated the cathode. Some of the large horizontal cracks in the center of the ceramic were filled with potassium. No noticeable potassium attack of the cermet was observed.

Two thermocouples were found in this sample. The first thermocouple, located at F, was 1.9 mm below the mesh-copper interface. The second thermocouple is shown at G. The thermocouple at F was located at the surface of the

cathode. This thermocouple, in operation throughout the entire test, measured a maximum surface temperature of 1865°K . The metal around the head was in contact with the ceramic castable.

The ceramic around the thermocouple at F was two-phased. The lighter phase was mostly iron with some magnesium and aluminum. The darker phase was mostly magnesium with some iron. In this area no potassium was found in the castable. Potassium was only found along the interface between the castable and the MAFF. The platinum was porous. This porosity was due to iron interactions. Precipitates of metallic iron were found in the platinum. Small amounts of the platinum were found dispersed throughout the castable in the higher temperature areas.

The upstream insulator had a major crack at H. The surfaces looked like fracture surfaces and not reaction surfaces. Although potassium was found in the crack, no evidence of potassium interaction or penetration of the insulator was found. The attachment of the cathode to the insulator at high temperatures and the expansion of the cathode because of cracking may have resulted in the massive crack in the insulator. Potassium in the crack indicated crack formation during operation, but the size of the crack was much smaller than shown in the micrograph.

Between the crack and location I in Figure 9 the insulator was generally single-phased without measurable potassium ($<0.5\text{ wt\%}$) except along the upstream side. On the upstream side at the area around the large vertical crack, small precipitates of LaCrO_3 ($>5\mu$) were found in the grain boundaries. The precipitates ($>5\mu$) were only found in the insulator in this location.

A second phase developed between I and J. At J, the second phase, which was mostly CSZ with some iron and small amounts of lanthanum and aluminum, covered 40% of the area. Near the plasma interface, the CSZ phase occupied 5% of the area and was located at the grain boundary. The magnesium-iron phase covered 40% of the area; the iron-contaminated spinel filled the rest of the area. Potassium was found throughout the area. The immediate surface of the insulator was covered with CSZ. Iron-contaminated spinel was found below this surface layer with the CSZ along the grain boundaries.

Cathode 107. Cathode 107, shown in Figure 10, was more severely eroded than either cathode 105 or 106. The enhanced erosion of the downstream area may have been due to the erosion of the adjacent downstream electrode cathode 108. The sample had many horizontal cracks. Many of the smaller cracks around the area of large cracks were intergranular. Cracking occurred between the ceramic and the cermet. Neither the cermet nor the interface between the cermet and the metal was cracked.

Potassium was found throughout the sample. Potassium concentrations were found along the upstream edge of the electrode. The potassium migrated into the crack between the ceramic and cermet and into the ceramic portion of the cermet.

The microstructural changes on this polished surface were different than for cathode 106. The microstructure of cathode 106, as seen on the polished section, may not reflect the remainder of the bulk because of the influence of the thermocouple. The microstructure of cathode 107 reflects the bulk and not the influence of the thermocouple. This microstructure was similar to that seen in cathode 105.

The EPI was affected in some areas by CSZ contamination from somewhere in the test stream, probably the nozzle area. The material at A comprised two interconnecting granular phases: CSZ and MgAl_2O_4 with a trace of iron. Upstream at B no zirconia was found, but at C, above the insulator, CSZ was found along the grain boundaries.

The EPI at B, the area that showed the least erosion, was two-phased with iron-depleted MgAl_2O_4 as the matrix. The second phase, found both as isolated grains and at grain boundaries, contained magnesium and iron.

In the more highly-eroded EPI, iron-depleted spinel was not found. This phase was not found because: 1) the surface eroded at such a rate as to limit the amount of time the surface was exposed to the plasma, and 2) the surface temperature may have been low enough to severely reduce the vaporization kinetics.

Two phases were found in the EPI at D: 1) MgAl_2O_4 with no depletion and 2) an interconnecting granular oxide phase containing magnesium and iron

(located mostly at the grain boundaries). At E the two phases were: 1) MAFF with no potassium and 2) MAFF with some iron depletion and potassium. At F the cathode was two-phased: 1) MAFF with a little potassium and 2) potassium, iron oxide and a little aluminum located at the grain boundary. The overall potassium content of this two-phased area was high compared to most of the areas.

The microstructure at G had a mottled appearance because of the intermixing of two phases: 1) MAFF with potassium and somewhat depleted in iron and 2) MAFF without iron. At 1000X a third granular phase was occasionally found: iron-contaminated CSZ.

A little potassium was found at H. The microstructure contained two phases: 1) MAFF and 2) a nonmetallic iron-rich phase (10% of area). At K the two phases were 1) MAFF depleted in iron and 2) aluminum and potassium with small amounts of magnesium and iron. The magnesium-iron oxide phase was not found.

At J the matrix was MAFF with some potassium. The second phase located at the grain boundaries was mostly potassium with some iron. At K the material was single-phased MAFF with some potassium at the grain boundaries and in cracks and some pores.

The insulator between cathodes 107 and 108--i.e., the plasma-sprayed insulator for cathode 108--was single-phased between the insulator base and L and contained MgAl_2O_4 with no measurable potassium. At M in the reaction area between the electrode and insulator, two phases were found in the insulator: 1) MgAl_2O_4 with iron and 2) an oxide containing yttrium, cerium, hafnium and zirconium. Near the plasma surfaces the two phases were: 1) MgAl_2O_4 and 2) an oxide containing zirconium, cerium, and yttrium with a small amount of hafnium. The insulator was also two-phased at the plasma interface near to cathode 108. These phases were: 1) oxide containing aluminum and cerium with a small amount of magnesium and iron, and 2) potassium at the grain boundaries.

The upstream insulator contained two phases near the plasma surface. The second phase was CSZ and was found as grains along the grain boundaries. At M

the material was single-phased (MgAl_2O_4 with some iron contamination) with enlarged grain boundaries. Potassium may have enlarged the boundaries in this area. The crack in this insulator may have been due to the expansion of the cathode and the attachment of the cathode to the insulator near the hot surfaces.

Electrode-Insulator Combinations No. 7 and 8

The electrode constituting electrode-insulator combination no. 4 were fabricated by Argonne National Laboratory (ANL). The specific compositions of the anodes and cathodes are listed below:

- 9.7 mole% Y_2O_3 · 16.3 mole% CeO_2 and 74 mole% HfO_2 attached to nichrome metal mesh for anodes 208 and 210 and cathodes 108 and 109
- 18 mole% CeO_2 · 82 mole% HfO_2 attached to Hoskins 875 metal mesh for anode 209 and cathode 110

The insulators, composed of MgAl_2O_4 , were applied to the sides of the electrodes by plasma-spraying.

Anodes for Combinations No. 7 and 8. The pretest anode 210 was severely cracked. Anode 209 had a small piece missing on the downstream side close to the outside edge. After the test, not enough ceramic remained to determine if the pretest cracks healed. The pretest anodes were multicolored, having green, blue, and buff hues, indicating a more reduced oxidation state than the posttest buff color.

In the posttest samples, the anodes showed excessive ceramic loss, as seen in Figure 1. Little ceramic remained on the anodes or the insulators. At least with anodes 208 and 209 the metal mesh was exposed to the plasma. Visual observation of the anodes after testing showed that the loss of ceramic extended over about 60% of the surface on all three anodes. The anodes were more eroded than the insulators, resulting in a valley-like appearance of the anode between the insulator. Because of the general leveling effects of the plasma, excess erosion of an anode led to enhanced erosion of adjacent insulators or anodes. For all three anodes, the wire mesh remained attached to the copper leadout. Not enough ceramic remained on the three anodes to evaluate the integrity of the ceramic metal interface.

The untested 18% CeO_2 ·82% HfO_2 sample was three-phased. The phases were uniformly distributed and of about equal area. Microstructure islands that were present were essentially one-phased material and were surrounded by smaller grains of two separate phases. Some interactions occurred between the anode and the Hoskins metal during fabrication.

The untested 9.7 mole% Y_2O_3 ·16.3 mole% CeO_2 and 74 mole% HfO_2 anode was three-phased. The microstructure appeared to be a mixture of the two-phased CHF and yttria. The third phase was randomly distributed as granular particles. The insulator was not chemically bonded to the anodes. A separation existed along the insulator-electrode interface. The insulator appeared to have some bonding along the mesh-ceramic interface. The anode was severely cracked in both the ceramic area and in the metal mesh area. In the mesh areas the cracks went around the perimeter of the metal and continued through the ceramic.

Anode 208. Anode 208, Figure 11, was severely recessed with little ceramic remaining. The remaining ceramic in anode 208 had some contamination from both MgAl_2O_4 insulators and MAFF. These two materials flowed over from the immediately adjacent upstream electrode and insulator. The uncontaminated electrode material was polyphased with four identifiable phases at 250X magnification. This material was all restructured and did not resemble the original microstructure.

At A, the metal mesh eroded almost to the copper. The remaining metal in this region was not oxidized and appeared to be the original metal. Upstream from this highly-eroded area at B some of the mesh appeared to have fused or bonded together. The heating required for this bonding could be due to exposure to the hot plasma or arcing. The outer layer of this bonded mass had a reaction zone with apparent oxidization. Small pieces of metal were found in the ceramic immediately above the bonded mass. Above the small pieces of metal was a nonmetallic phase resembling the shape of the metal inclusions. This phase was probably oxide nichrome.

The insulator on both sides of the anode was severely corroded. The insulator reaction zone was in the area of the metal mesh. This reaction zone

was full of potassium and may have led to the low resistances measured by Westinghouse between anodes 207 and 208. The insulator above this corrosion zone showed some interaction with the electrode but remained intact. Some potassium was found in the mesh region. No interaction was seen between the potassium and the nichrome mesh.

Anode 209. Anode 209, shown in Figure 12, also showed large amounts of erosion. The metallographic section cut through an area where a ceramic piece protruded above the metal matrix. The ceramic protrusion in the center of the electrode was real and not a result of material loss during metallographic preparation. The insulator undoubtedly offered some protection from plasma erosion for the electrode. The center protrusion was a ceria-hafnia compound with gross microstructural changes. The top layer was dense within an area of large porosity and an area of many small pores--some apparently filled with seed. The surface of the protrusion was a light phase, like the matrix, with a medium-dark phase on the grain boundaries. Farther back into the intrusion were some smaller grains of matrix with a second medium phase in larger grains. The second phase represented 55% (90% of the area); the light phase in the form of small grains represented 40%; the darker third phase, randomly distributed as grains, constituted the remaining 5%.

The Hoskins 875 metal mesh recessed below the protrusion. The maximum mesh height was 0.25 cm, compared to an original height of 0.43 cm. The metal mesh closest to the plasma surface oxidized.

Hafnia-based electrode material was found on the upstream insulator, probably from anode 208. Interaction occurred between this electrode material and the insulator. The upstream insulator showed excess corrosion close to where the anode contacted the copper cooling block. Potassium was found in this reaction area. The second phase including potassium was found in the grain boundaries of the insulator in this region. One possible explanation for the high-reaction zone is the nonuniform density generally characteristic of plasma-sprayed materials. Areas of porous insulator may have been initially deposited in the high corrosion area during fabrication. These porous regions acted like a sponge to soak up potassium. Of course, the greater the reaction surface area, the greater the amount of reaction.

The downstream insulator was also covered with electrode material. This material probably came from anode 209. This electrode material also interacted with the insulator. The electrode material penetrated along the grain boundaries of the insulator, forming a second phase.

Anode 210. For anode 210, shown in Figure 13, the ceramic eroded more uniformly than for anodes 208 and 209 to the level of the mesh. The remaining ceramic was porous, with large pores surrounded by dense grains. The ceramic that penetrated the nichrome was severely cracked. The ceramic had three dominant phases and two minor phases.

The metal mesh close to the plasma surface oxidized and no longer had a metallic appearance. Further examination of wires in the sample showed the oxidation reaction boundary moved along the grain boundaries, then into the grains. The oxidation reaction began on the outside of the wire and worked toward the inside, leaving a reaction boundary layer.

A small reaction occurred between the downstream anode and the insulator. The insulator was raised off the copper because the electrode ceramic lifted off the metal mesh.

Cathodes for Combinations No. 7 and 8

The microstructure of the pretested samples were similar to those of the respective anode compositions. All the cathodes had microscopically observable cracks in the ceramic but not in the insulator. The pretest cathodes were also multicolored with blue, green, and buff hues, as were the anodes. Like the anodes, the posttest cathodes were buff-colored. All three cathodes had less material loss than the respective anodes. Each of the cathodes had more extensive potassium penetration and interaction than the anodes.

Each of the cathodes was severely cracked. Cracking was found around the metal mesh. In all the samples, the ceramic that penetrated the metal mesh cracked. The metal mesh maintained contact with the copper.

Cathode 108. Cathode 108, pictured in Figure 11, underwent major microstructural changes above C. The EPI consisted of large dense grains. These grains were hafnia-ceria with some ceria depletion. (Some grains showed enhanced ceria depletion at the immediate EPI). No phase containing Y_2O_3

was found between the EPI and D. The boundary between grains was wider than the initial matrix. The wide boundaries gave an impression of isolated grains when viewed with the SEM. Potassium was found along the grain boundaries. The widening of the grain boundaries was due to both potassium attack of the hafnium-cerium grains and the removal of the yttria.

A second phase appeared at D. This phase was an oxide containing yttrium, hafnium, and cerium with some silicon impurity. The phase covered about 30% of the area. Analysis of different grains of this single phase yielded the same composition, indicating that it was a single-phased ternary compound. The matrix at E was a Ce-HfO₂ compound; the oxide containing yttrium, hafnium and cerium was not present. The second phase in this area was the same as the untested sample--i.e. Y₂O₃.

During hot-pressing, little reaction occurred between the yttrium and the Hf-Ce matrix. During the proof test, however, yttria did react with the Hf-Ce matrix, forming the oxide containing yttrium, hafnium and cerium at the higher-temperature regions above D. Isolated grains of Al₂O₃ were occasionally found throughout the area between C and D. These grains were probably from contamination during fabrication.

In all the Hf-Ce-Y cathodes, a band of more dense ceramic was found in the center portion of the metal matrix (see F in Figure 1). This ceramic had a buff color different than the remainder of the electrode. The buff-colored area was two-phased; the darker phase (20-30% of the area) was mostly cerium and yttrium with some HfO₂, and the second phase was mostly hafnium with littler cerium and yttrium. These two phases were different from the rest of the sample. Argonne National Laboratory stated that the entire cathode was fabricated from the same powder. During the fabrication process particles of the initial starting powder that were close in composition to the two phases in the buff-colored zone separated from the remainder of the powder and deposited in this area. This was apparently due to differences in density and to compositional inhomogeneities of the starting powder. The ceramic was severely cracked even after fabricating.

Interactions occurred between the electrode and insulator. The insulator had penetrated the electrode along the grain boundaries. Some of the

electrode material had penetrated into the insulator. Ceria was found throughout the hotter portions of the downstream insulator. Ceria was also found at G. It had formed a compound with aluminum. This compound contained a small amount of magnesium and iron. Some potassium was found at the grain boundaries.

In the metal wire-ceramic portions of cathode 108, metal was found in the ceramic surrounding the metal mesh wires. Some potassium was found in the same areas as the metal. This metal was only found in cathodes 108 and 109. (The amount of metal in cathode 109 was much less than in cathode 108). Three possible mechanisms for this metal formation are: 1) formation during fabrication because of interactions between the metal and ceramic or the reduction of the ceramic, 2) formation during operation because of interactions between ceramic and metal, or 3) formation during operation because of the reduction of the ceramic from ionic transference of current. Not enough information is available to determine the mechanism.

At E, immediately above the metal wires, some chrome and a much smaller amount of nickel were found in the Hf-Ce electrode material. A small amount of potassium was found in this area. No hafnium, cerium, or yttrium was found in the metal wires.

Cracking was found throughout the sample. Many small cracks were found that do not show on the figure. A major crack was found at E along the top layers of the metal mesh. A crack in this location could lead to eventual separation of the ceramic from the metal. Cracking inside the mesh, such as at D, may not significantly degrade the mechanical strength, but allows passage for potassium. The cracking in the mesh was a result of differences in thermal expansion between the ceramic and metal and the relative volumes of the two materials. The sample also was quite porous. Most of the electrode grains appeared to be separate from the adjacent grains except for a few areas of contact. Potassium was not found in these enlarged grain boundaries except where the boundaries were in close proximity to crack or other free surface. Potassium was found in the cracks at C and H. The many small, intergranular cracks found between D and the EPI generally did not contain potassium.

Potassium did not significantly degrade the material in the bulk ceramic as in the case of the spinel-based electrodes. Potassium buildup along the downstream interface between the cathode and insulator at I resulted in enhanced potassium attack in both the cathode and ceramic in this region. No evidence of potassium attack in the nichrome was observed, although, as previously mentioned, potassium was found in the areas where the wire had penetrated the ceramic. Potassium could have partially caused this penetration.

Cathode 109. Cathode 109, shown in Figure 12, had a restructured zone between location A and the EPI. The restructured zone not only had a new phase, but also was severely cracked. The cracks at A generally outline the interface where the new phase formed. This phase contained potassium, cerium and aluminum.

The microstructure near the EPI was two-phased: 1) MgAl_2O_4 and 2) ZrO_2 containing some HfO_2 . Below the two-phased area was the phase that dominated the rest of the EPI below the surface. This phase was HfO_2 , containing both cerium and yttrium.

Another area of the EPI near the upstream edge at D had three phases: 1) ZrO_2 with small amounts of HfO_2 , 2) MgAl_2O_4 , and 3) the matrix $\text{HfO}_2\text{-CeO}_2$ compound. The entire EPI was covered with ZrO_2 . This zirconia interdiffused with the hafnia. No signs of stress cracking were found at interfaces between the zirconia coating and the hafnia.

About 0.5 mm below the EPI, zirconia was found only as a few isolated grains. The hafnia was depleted in cerium and contained only small amounts of yttrium. A new phase was found containing potassium, aluminum and cerium. The new phase was located at the grain boundaries, and in some areas covered up to 20% of the polished surface. This phase was found only in an area between 0.5 mm and 1.2 mm below the EPI. The grains in this band had wide grain boundaries and were more porous than the untested material.

The buff-colored denser ceramic in the metal mesh was similar in composition to the buff area of cathode 108, except this area had three phases: 1) a major phase of HfO_2 with a little cerium and yttrium, 2) a second oxide phase consisting of cerium and yttrium with some hafnium, and 3) a third oxide phase (5% of the area) consisting of aluminum with some hafnium and cerium.

Cracks were found throughout the ceramic. A series of cracks developed along the area at the top layer of metal mesh. Potassium was not found along these cracks. Cracking also occurred in the metal mesh area. Some potassium did penetrate these cracks.

Potassium penetrated the cathode at B. Other than this area of gross potassium penetration, the remainder of cathode 109 was relatively potassium-free except in the area around cracks, as previously mentioned. Less potassium was found in this cathode than in the spinel electrodes and in cathodes 108 and 110. Except for a small amount of C, the upstream insulator was not found in this polished section, since most of it was removed to attach the thermocouples. The castable used to fill the thermocouple cavity was saturated with potassium. The high concentration of potassium in the castable led to the potassium attack of the electrode at B. Much of the castable material reacted with the potassium and would not polish, and therefore could not be examined. The only part of the upstream electrode that remained was found at C. The small amount of insulator at C had reacted with potassium mainly because of grain boundary interactions.

The downstream insulator contained potassium. This potassium concentration was partially due to the gross erosion of cathode 110, resulting in large potassium concentrations in its insulators. A potassium bridge existed between cathodes 109 and 110, which may have led to the low measured values of interelectrode resistance.

The thermocouple shown in cathode 109 pulled out of its hole prior to potting in Maraset. It is not clear whether it was pulled out on channel disassembly or was that way during channel testing.

Cathode 110. Cathode 110 (Figure 13) was severely eroded. The erosion did not leave a smooth surface. The erosion pattern produced axial valleys perpendicular to the flow of the plasma and separated by clusters of material. Figure 13 shows the tip of a cluster at A above an eroded area at B. At C, near the EPI, two phases were present: 1) the matrix containing HfO_2 with a trace of cerium^(a) and 2) grain boundary deposits containing aluminum, iron and cerium with a trace of hafnium.

(a) The depletion of cerium at the EPI was found in both the anodes and cathodes; yttrium depletion was slight, if any.

A eutectic-type structure developed at D at the EPI on the tip that had projected over a valley where the severe erosion had occurred. This eutectic structure was not found on any other electrode. The eutectic implied melting. This is the only good indication of melting on any of the hafnia-based electrodes. The eutectic was only found in a narrow surface layer, and represented the molten material that resisted the stresses of the plasma because of capillary and surface tension. The high heating of this localized region could be due to the plasma and/or arcing. This eutectic structure was intermixed with grains of the HfO_2 containing a trace of cerium. The dark oxide phase in the eutectic contained aluminum, iron and cerium and some hafnium. Three lighter oxide phase compositions were identified: 1) hafnium and cerium with some zirconium and a trace of iron; 2) hafnium, aluminum, cerium, and iron; and 3) hafnium, cerium, and iron. Each of the compositions of the light phase were grouped and did not intermix with the other phases. A second eutectic composition was found at C. The two oxide phases contained 1) magnesium, aluminum and iron and 2) hafnium with a little cerium.

Below the EPI at E there were two phases with a granular second phase of MgAl_2O_4 and iron scattered in the HfO_2 -Ce matrix. There were two other phases at F, an area farther from the electrode-insulator interface: 1) the HfO_2 - CeO_2 matrix containing some iron and 2) an oxide of potassium, silicon and aluminum with some iron and hafnium. This second phase was located along the grain boundaries. Below F, at G, the grains were more broken up than in other locations. Potassium was found along the grain boundaries. The Hoskins 875 metal wires in this area oxidized. The oxidized wire had two phases: 1) iron with some chromium and aluminum and 2) chromium with a trace of iron. Most of the wires were either fully or partially oxidized up to the buff-colored region starting at H. The buff-colored ceramic comprised two phases: 1) the matrix of HfO_2 with a trace of cerium and 2) a second granular oxide phase of aluminum with lesser amounts of hafnium and cerium.

The Hoskins 875 metal oxidized. Hoskins 875 consists of 72 wt% iron, 22 wt% chromium, 5.5 wt% aluminum, and 0.5 wt% silicon. Brown coloration from oxidized iron was found on the surface of the cathode around this highly

eroded area and on a portion of the upstream electrode, cathode 109. The circular oxide at C was totally oxidized metal wire.

The darker area in the center of the sample, as at I, is a region of severe potassium attack. Potassium was found along the enlarged grain boundaries. The overall SEM analysis of this area showed high concentrations of hafnium, cerium and potassium, with small amounts of iron.

The excessive erosion led to severe potassium penetration of the wire mesh area. Potassium did not appear to be reacting with the metal wires. No potassium penetration of the unoxidized wires was observed. Potassium attacked and penetrated the wires once they were oxidized. Potassium did not react with the buff-colored material around the wires, although it did penetrate the cracks.

PROOF TEST NO. 2

The second proof test was conducted on November 17-18, 1977. The test consisted of four phases: 1) startup and checkout of the channel, 2) electrical tests of the channel and the electrodes, 3) operating life test including a midpoint electrical test of the channel and the electrodes, and 4) shutdown. The electrodes and insulators were exposed to the seeded plasma for a total of 21.3 hr. The goal was to have the current density on each electrode at 1.0 A/cm^2 . All the electrodes except 101 and 201 (0.6 A/cm^2) and 102 and 202 (0.2 A/cm^2) operated at 1.0 A/cm^2 .

After the proof test the channel was disassembled and the electrodes and insulators were visually examined. The electrodes initially appeared to be in good condition, with few gross differences between the anodes and cathodes. During the removal of the top insulator wall, water was accidentally spilled on both the anodes and cathodes. Within 17 min of the spill, cathodes 110-112 began to show the effects of hydration by swelling and crumbling. After the spill a heat gun dryer was used to evaporate the water. Most of the water had evaporated in 20 min. After about 20 min hydration effects were noted on cathodes 104-106. No hydration effects were seen on cathodes 101-103 and 107-109. A small amount of swelling was observed on anodes 210 and 211 30 min after the spill. Hydration could have occurred in the other electrodes, but

not to an extent that would result in the gross breakup of the electrodes. These more subtle effects may be seen on a polished surface as extensive cracking and grain boundary interactions.

After visual examination the samples were placed hot face down into a pan of Maraset mounting media for potting prior to sectioning. The anode wall was cut in half and one-half was sent to PNL. At PNL the half sample was cut longitudinally 3/8 in. from the inside surface. The cutting was done with a SiC wheel using kerosene as the coolant and lubricant. The newly exposed surface was polished for microscopic examination. The cathode wall was polished as-received with the polished face 35 mm from the insulator sidewall.

The electrodes and insulators tested are summarized in Table 2. Density measurements shown in the table were made by Westinghouse. Cross sections of both the anodes and cathodes are shown in Figure 14. No areas of excessive erosion were found in either the anodes or cathodes.

After polishing and examination, various observations were made. The cathodes had degraded more than the anodes. The rapid hydration of the cathodes hindered the direct comparison of the microstructural degradation between the anodes and cathodes. The rapid hydration of the cathodes as compared to the anodes does indicate either more potassium or lanthanum oxide at grain boundaries, cracks and interconnecting surfaces. High-temperature interactions occurred between electrodes and insulators.

All of the attachments between the electrodes and either the copper or the nickel metal mesh had problems in terms of structural integrity. The epoxy bonds separated from the ceramic but adhered to the copper, which was a reversal from the first proof test. The plasma-sprayed Ni-Mo-Al metal on the plasma-sprayed electrodes separated from the copper surface. Stress in the ceramic at the ceramic-metal bond at the nickel mesh resulted in cracks in the ceramic.

The anodes and cathodes did not show the excessive wear or microstructural changes associated with overheating caused by design problems. No electrode material was found to have flowed over the downstream electrodes.

The results of the microstructural analysis are grouped by the electrode processors (Table 1). Within each group, anodes are described separately from

TABLE 2. Electrodes and Insulators for Proof Test No. 2

Electrode Insulator Combination	Channel Location	Material	Source	Fabricator	Fabrication Technique	Density g/cm ³ (% TD)	% Total	Porosity		Attachment Method
								% Closed	% Open	
9 Electrode	101, 103 and 201-203	Graded LaCrO ₃ to ZrO ₂ cap at EPI		Eagle-Picher	Hot-pressed, layered	6.15 (96%)	4.00			Epoxy to Copper
Insulator		MgO	Trans Tech	Westinghouse	High-temper- ature sinter	3.51 (98%)	1.96	1.71	0.25	
10 Electrode	104-106 and 204-206	Graded LaCrO ₃ to ZrO ₂ cap at EPI (nickel leadout)		APS	Plasma- sprayed, layered structure					Epoxy to Copper
Insulator		MgAl ₂ O ₄	Trans Tech	APS	Plasma- sprayed spinel					
11 Electrode	107-109 and 207-209	La _{0.95} Mg _{0.05} CrO ₃ + 30 w/o 2Y ₂ O ₃ -88ZrO ₂	General Refractory Norton	Westinghouse	Hot-pressed at 2.07 x 10 ⁷ Pa and 1893°K	6.17 (93%)	7.0	4.96	2.04	Epoxy to copper
Insulator		MgAl ₂ O ₄	Trans Tech	Westinghouse	High-temper- ature sinter	3.15 (98%)	2.01	1.93	0.08	
12 Electrode	110-112	La _{0.95} Mg _{0.05} CrO ₃	General Refractory	Westinghouse	Hot-pressed at 1893°K	6.38 (96%)	3.94	3.93	0.01	TiCuSi1 brazed to nickel mesh
Insulator	210-212	MgAl ₂ O ₄	Trans Tech	Westinghouse	High-temper- ature sin- tering	3.51 (98%)	2.01	1.93	0.09	

the cathodes. Within either the anode or the cathode description will be a more detailed description based on the SEM examination of the downstream electrode and insulator. This downstream electrode should have the least contamination from dissimilar upstream electrodes.

Electrode-Insulator Combination No. 9

The electrodes used in electrode-insulator combination no. 1 were fabricated by Eagle Picher. These were hot-pressed, graded electrodes comprising four zones or layers. The base layer (zone 4) was lanthanum chromite. Dense islands of chromite were surrounded by a porous, smaller-grained chromite matrix. The chromite was two-phased, with a darker second phase intermixed with the lighter matrix phase. The lanthanum chromite in all three zones was two-phased. Zone 3 was a mixture of the lanthanum chromite and a small amount of zirconia. Zone 2 had a greater proportion of zirconia. In this zone dense zirconia grains were surrounded by a more porous chromite. Zone 1 consisted of dense zirconia. The zirconia was single-phased. Both zones 1 and 2 were severely cracked. The electrode blocks mounted on the copper had chips of the top two layers missing in various locations.

Visual examination of the anode and cathode surfaces of those electrodes after the test showed the crazing patterns expected with this type of severe cracking. These posttest electrodes were as severely cracked as the untested specimens. The cracks in zone 2 in the zirconia extended into the chromite. The interfaces between each of the zones were relatively uncracked, with no evidence of separation.

The sintered MgO insulator was single-phased, with small pores generally at grain boundaries. The insulator was not well bonded, as shown by separations between grains on a fracture surface examined by the SEM.

Anodes for Combination No. 9

Anodes 201, 202 and 203 are shown in Figures 15 and 16, respectively. Anode 201 was the most severely eroded. Some of this erosion was due to erosion in the ceramic at the channel inlet. All three anodes retained portions of their caps. The anodes in zones 2 and 3 were more severely cracked than the untested anodes. The anodes had separated from the copper cooling blocks.

The separation occurred when the epoxy attached to the electrodes cleanly detached from the copper. The separation of the anode from the copper caused the insulator to crack. In general, severe potassium attack was not observed in the anodes, although potassium penetration was observed and will be discussed in the detailed description of anode 203.

Anode 203. Anode 203 (Figure 16) was examined in greater detail than were either anode 201 or 202. The anode contained all four zones. The downstream insulator was attached to the anode at the hotter temperatures. The parts of this insulator that were lower in temperature remained attached to anode 204.

Anode 203 was examined using the SEM. The area between the surface layers and the base of the anode (i.e., zone 4) consisted of two types of macro-islands--a dark island as seen at A, and a light island as seen at B,--surrounded by the matrix as pictured at C. The dark island comprised two phases: 1) LaCrO_3 with a high aluminum content and some chromium depletion and 2) LaCrO_3 that was more depleted in chromium than the first phase. The light island comprised LaCrO_3 and an oxide containing mostly chromium. The overall chromium content of the lighter island was higher than that of the dark island. The aluminum content of the dark islands was less than that of the light islands. The matrix around these islands was also two-phased. The phases were: 1) LaCrO_3 that was depleted in chromium and contained some aluminum and 2) an oxide containing mostly chromium with some magnesium and aluminum. This chromium-rich second phase was found even in the two-component regions of zones 2 and 3. This chromium oxide phase was larger in size and quantity in zones 2 and 3 than in zone 4. For example, the concentration of the chromium oxide in zone 2 was twice that in zone 4.

Also shown in Figure 16 is a higher magnification composite transversing zones 1 and 2 and part of zone 3. In zone 3 the dense grains of cerium-containing ZrO_2 at D were easily distinguishable from the more porous LaCrO_3 at E. The zirconia grains contained varying amounts of cerium. In general, cracks were found outlining the interface between the ZrO_2 and the LaCrO_3 . These cracks occasionally contained potassium. These cracks probably formed because of a thermal expansion mismatch between ZrO_2 and

LaCrO₃. In zone 2 the zirconia (F) also contains some lanthanum. The ZrO₂ grains closest to zone 1 (or those at the higher temperature) contained the most lanthanum. A porous area (G) separated zone 1 from zone 2. This porous region contained interconnecting porosity that was in contact with a free surface, since the pores were filled with Maraset. This porosity developed during testing. The pores were not likely attributable to the thermal expansion mismatch, which usually results in sharp cracks. The pores were probably from oxygen deposition at the interface, where the electrical conductivity changes from mostly ionic in the zirconia layer (zone 1) to electronic in the LaCrO₃ (zone 2). Because of the higher electrical conductivity and the increased concentration of the LaCrO₃ in the composite regions of zones 2 and 3, no porosity was found. At this interface the ionic species carrying the current through the zirconia (mostly oxygen) would concentrate. The extent of the porosity buildup at the interface attributable to oxygen could not be determined because the interconnectivity of the porosity might allow the excess oxygen to migrate back to the plasma stream. If the kinetics of oxygen migration from the sample were at least as great as oxygen migration through the porosity, no more porosity would develop. If the kinetics were slower, more oxygen deposits might occur in this interface region, with a resultant weakening of the interface layer and the separation of the cap from the remainder of the electrode.

In zone 2, even though much of the current was carried by the electronically conducting LaCrO₃, the ZrO₂ concentration was high enough so that some current also passed through the ZrO₂ grains. The same oxygen depletion at the hotter surfaces and deposits at the cooler surfaces of the ZrO₂ may have resulted in the stratified porosity seen in this zone (e.g., at H). The porosity was interconnected, as evidenced by the pores filled with Maraset. This porosity was distinguished from cracks by its smoother incurvature and more rounded appearance.

The interconnecting porosity was not found in zones 3 or 4. In zone 3 the zirconia concentration was considerably smaller, resulting in a greatly reduced amount of current transported by the ZrO₂.

Little chromium depletion of the LaCrO_2 was found in zone 2 other than that described for the multi-phased zone 4, whose phases appear even in this zone. The potassium found in zone 2 appeared to be in areas where the chromium concentrations were higher than average. No potassium was found in zone 1, even along the cracks.

The EPI for anode 203 was coated with grains of ZrO_2 containing calcium. This ZrO_2 was from upstream areas of the test facility such as the nozzle or the combustor. The calcium-containing ZrO_2 was also found along grain boundaries in both the upstream and downstream insulators.

After testing, both the upstream and downstream insulators were attached to the anode. The upstream insulator, composed of MgO , was attached only in the hot areas, as reflected by the location of the crack formed when the anode lifted away from the copper cooling block. In the interaction area, aluminum from the anode migrated into the matrix grains of the MgO , forming MgAl_2O_4 in some areas; ZrO_2 also migrated into the insulator, but formed deposits only at the grain boundaries. Little potassium was found in the insulator, and that only at the grain boundaries.

The downstream electrode was MgAl_2O_4 . At the high-temperature areas potassium and chromium migrated along the grain boundaries and either reacted with the spinel or partially hydrated, resulting in the separation of the MgO grains. On the downstream surface of the insulator closest to anode 204 a three-phased region was found. The phases were: 1) MgAl_2O_4 , 2) La_2O_3 with some aluminum and a small amount of chromium, and 3) Al_2O_3 with some lanthanum and a small amount of chromium. Potassium was found throughout this reactor zone.

Cathodes for Combination No. 9

Figures 17 and 18 show cathodes 101-103. The cathodes did not erode as much as the respective anodes. The cathodes did not have as much additional cracking and porosity in zones 2 and 3 as did the anodes. The cathodes showed more internal damage, especially from potassium attack, than did the respective anodes. Major areas of potassium attack are shown as the black areas on the micrographs. The higher concentrations of potassium at the cathodes also

resulted in severe attack of the interelectrode insulators. Potassium penetrated along the cracks between the electrodes and insulators, causing considerable potassium attack of the electrodes in zone 4 and of the insulators. The cathodes also separated from the copper cooling blocks. In some areas, epoxy remained on both the copper and the ceramic.

Cathode 103. Cathode 103 (Figure 18) showed the most potassium attack and interaction. Some of the potassium may have been from cathode 104, which was severely damaged. Part of the cap of this cathode separated from the rest of the electrode. The separation was due mostly to the posttest swelling of cathode 104. The cap was partially attached to the downstream insulator, which was attached to cathode 104. As cathode 104 expanded after being soaked with water on posttest disassembly of the channel, the downstream insulator lifted the portion of cap attached to the insulator. The downstream insulator remained with cathode 104.

The separation interface also showed the location of mechanical weakness from cracking. The separation crack was in the cerium-stabilized zirconia (zone 1) immediately above the interface between the zirconia and the zirconia-lanthanum chromite layer (zone 2). At the EPI, two granular phases were found: 1) potassium and silicon with some cerium-stabilized zirconia and 2) cerium-stabilized zirconia. This phase containing potassium and silicon was found mostly at EPI. Potassium was also found along cracks and in some pores.

In the cap (zone 1) the porosity not only coarsened but appeared to increase between the separation crack (at B in Figure 18) and the EPI. Some of this coarsening was due to the higher temperatures and the increased mobility of the vacancies. The additional increase in porosity near the EPI could have been due to 1) the migration of pores to the hotter temperatures (a phenomena commonly seen in porous ceramics annealed at high temperatures in temperature gradients), and 2) the generation of porosity because of the migration of oxygen (or other ionic species) resulting from the partially ionic transference of the cap material. This second mechanism was current- and current-density-dependent. The determination of the relative contributions that each of these two mechanisms makes to increasing the porosity cannot be determined from this proof test.

Six phases were found immediately below the separation interface at C: 1) cerium-stabilized ZrO_2 with some potassium but no lanthanum; 2) cerium-stabilized ZrO_2 ; 3) LaCrO_3 ; 4) ZrO_2 , containing LaCrO_3 with some chromium depletion; 5) ceria-doped ZrO_2 with some silicon and lanthanum (this phase was found along the grain boundaries); and 6) grain boundary granular deposits of oxides of chromium and zirconium. Farther into the layer, at D, only three phases were found: 1) LaCrO_3 (matrix), 2) Ce-ZrO_2 containing lanthanum as isolated islands, and 3) chromium oxide with a small amount of lanthanum (about 20% of the area). The dark cracks in this location all contain potassium.

At E, the interface area between zone 3 and zone 4, zone 3 had three phases similar to D: 1) Ce-ZrO_2 without the lanthanum found at the higher-temperature locations of zone 3, 2) LaCrO_3 with chromium depletion, and 3) an oxide mostly containing chromium with some lanthanum. Two phases were found immediately below E at F (zone 4): 1) LaCrO_3 (matrix) and 2) potassium chromium compound LaCrO_3 at the grain boundaries containing some lanthanum and aluminum. The grain boundaries were enlarged where this potassium-chromium compound was found.

The interface between zones 3 and 4 was porous. Many "isolated" grains were found with considerable potassium along the enlarged grain boundaries. This interface was not well bonded and showed considerable cracking. Since these cracks contained potassium and the potassium had severely interacted with the LaCrO_3 , they obviously occurred during the test.

At G, the aluminum-doped LaCrO_3 contained considerable potassium. Potassium was also found along grain boundaries and in the cracks. The phase that contained mostly chromium was not found in this area, nor in the remainder of the sample between this area and the interface area close to the copper. The remainder of the matrix between G and the copper interface was the polyphased mixture similar to the untested electrode except for occasional potassium deposits along the grain boundaries.

Like the other insulators between cathodes 101, 102 and 103, the upstream insulator was severely attacked by potassium. The attack was mostly found in the lower part of the insulator and not at the hotter areas. At the plasma

interface H two phases were found: 1) matrix grains of MgO and 2) calcium-stabilized zirconia along the grain boundaries. The zirconia was from the upstream components and not from the capped electrodes. No potassium was found in the surface areas.

At I, near the reaction interface, no zirconia was found along the grain boundaries. The grain boundaries occasionally contained LaCrO_3 , especially along the grains near the electrodes. At the interface between the top and bottom portions of the insulator at J, oxides of magnesium, chromium and potassium were found. The potassium and chromium were found together along the grain boundaries of the MgO matrix. The grain boundaries were enlarged in this area.

The lower insulator had swelled as shown by its relative width compared to the essentially untreated upper insulator. The swelling may have been due to the hydration of either potassium or lanthanum compounds. The grain boundaries of the MgO matrix in this reactor zone became enlarged. Areas were found with the grains missing because of an apparent separation of the grain from the surrounding neighbors resulting from enlarged grain boundaries. Examination of untested sibling samples did not reveal second phases along the grain boundaries. The MgO contained silicon in the matrix; enhanced concentration of the silicon along the boundaries was not observed. Elements with atomic numbers lower than 8 cannot be analyzed using the SEM; consequently, if a material such as lithium were added as a sintering aid it would not be detected. Lithium at grain boundary would make the grain boundaries quite reactive and highly susceptible to potassium attack. Enhanced potassium penetration could result from poorly bonded grains caused by inadequate sintering or porosity buildup along the grain boundaries. The samples were considerably porous along the grain boundary. The penetration of potassium along the grain resulted in the exposure of many surfaces to potassium attack. For better potassium resistance, the porosity along the grain boundaries must be reduced, the use of sintering aids must be reduced, and the grain size must be increased. An improvement of the potassium resistance is necessary prior to using the sintered MgO as insulators for cathodes in the U-02 phase III tests.

Electrode-Insulator Combination No. 10

Anodes 204, 205 and 206 and cathodes 104, 105 and 106 were fabricated by APS Industries of zirconia graded to lanthanum chromite graded through a nickel-molybdenum-aluminum composition to a nickel-plated copper cooling block. The insulator, MgAl_2O_4 , is plasma-sprayed on all four sides, completely covering the sides of both the ceramic electrode and the copper cooling blocks.

No untested sibling pieces were given to PNL for examination; consequently, it is not possible to describe the uniformity of microstructure, microstructural changes, degree of cracking, adherence of the insulator to the electrode, or relative porosity changes. Some information can be inferred by examination of the posttest samples and the macrophotographs of the EPI prior to testing. The following general observations on the untested samples were based on examination of the macrophotographs. Cracks were found at the interface between the electrode and insulator. Apparently the insulator was not well bonded to the electrode. Slots were placed in the electrode to be filled by the insulator and promote better adhesion. The cracks seem to continue through the electrode material found in the slots, apparently negating the effect of the slots. The EPI did not appear cracked or crazed.

Interpretation of the posttest examination of both the anodes and cathodes was difficult because of excessive hydration and destruction of both the anodes and cathodes on contact with water spilled during disassembly. Hydration of the cathode occurred prior to hydration of the anodes and produced more apparent damage on cathodes than anodes. However, the rapid hydration indicated both a greater amount of potassium and/or lanthanum and a greater ease of penetration of water into the sample than for the other electrodes. Cathode swelling appeared to be due to the hydration of both potassium and lanthanum. The anode swelling was mostly due to lanthanum.

The two upstream anodes lost most of their surface zirconia caps because of hydration. Anode 106 returned most of its cap even after hydration. The caps on both the anodes and cathodes were attached to the electrodes before the hydration. The caps on the cathodes were also lost after hydration. The cathodes were more severely hydrated than the anodes. The massive cracks that

appeared in the cathodes continued through the adjacent insulation. The severe cracks on the cathodes were not observed on the anodes. Since few macro-cracks were found on the anode, the swelling was generally due to hydration of surface layers more than the massive bulk hydration of the cathode.

Some interactions were found between the electrodes and insulators; for both anodes and cathodes, cracks in the electrode continued through the adjacent insulators. No gross flowing of electrode material over the insulator was observed.

The nickel separated from the copper at the copper-nickel interface on the anode. This separation did not occur on the cathode, even though some cracks were found at the interface.

Anodes for Combination No. 10

Anodes 204, 205 and 206 are shown in Figures 19 and 20. The anodes were not as severely damaged as the respective cathodes. As shown in Figure 19, only a small amount of the zirconia cap A remained. All of the ceramic to B had hydrated. Cracks occurred at C between the copper and the electrode.

Anode 206. A cross section of anode 206 is shown in Figure 20. Swelling in the sample resulted in the separation of the deposit layers (e.g., at A). In this area little potassium was found in the grain boundaries. The grain boundaries contained lanthanum; much of the swelling was due to lanthanum hydration. The swelling enlarged the grain boundaries; consequently, the microstructure looked like isolated grains separated by large grain boundaries. The high chromium-containing second phase was not found in the swelling areas.

At the apparent EPI at B, the grain boundaries were not as severely attacked. Little grain boundary enlargement or grain separation was observed. The actual EPI (ZrO_2 cap) was missing. The final thickness of the ZrO_2 cap is unknown. During the test the area at B may have been hot enough to change the initial plasma-sprayed microstructure. The material in this area was more dense and had larger grains than found farther within the electrode. The microstructural change could have been caused by sintering and grain growth. The area also had changed in chemical composition. Instead of LaCrO_3 with a chromium-rich second phase, the area consisted of these three phases: 1) chromium-depleted LaCrO_3 , 2) lanthanum oxide containing some

aluminum, and 3) lanthanum oxide containing silicon and aluminum. The lanthanum oxide grew into the LaCrO_3 from the grain boundary as the chromium was removed from the grain either by a potassium leaching mechanism or a diffusion-vaporization mechanism. The surface lanthanum oxide layer did not hydrate because of a lack of moisture in this area; the area was immediately exposed to the heat gun dryer after the accidental water spill. Water in the interior of the electrode would have had a longer residence time before exposure to the effect of the heat gun dryer, consequently resulting in hydration of the lanthanum oxide.

The dense areas at C in the interior of the sample did not contain lanthanum oxide deposits along the grain boundary. However, the microstructure had been altered and differed from the dense areas at D. The microstructure at C consisted of two phases: 1) chromium-rich LaCrO_3 (10% of area) and 2) slightly chromium-depleted LaCrO_3 . The chromium oxide second phase found at D was not present.

At D the microstructure probably represents the untested microstructure. The microstructure shows grains separated by porosity. On a macroscale, the porosity was in layers that separated layers of more dense ceramic. Each layer represents a pass of the plasma sprayer. The porosity between the layers provided easy paths for potassium and moisture penetration. The plasma-sprayed materials included two phases: 1) LaCrO_3 and 2) an oxide containing mostly chromium (5-10% of area). Near the base of the electrode E, where layers of nickel and ceramic alternate, a third phase (5% of area) was found consisting mostly of Al_2O_3 .

Separation of the electrode from the copper at E occurred at the nickel-copper interface. The only nickel remaining with the copper was that left in the copper grooves.

The insulator was porous with some preferred orientation of the cracks in the direction of plasma spraying. Potassium was found in some of these cracks and along some grain boundaries. Some of the spinel grains also contained potassium. At the higher temperatures the insulator reacted with the LaCrO_3 . Part of the insulator was missing because of this interaction. At these

higher temperatures LaCrO_3 penetrated along the grain boundaries and the porous area. Grains of LaCrO_3 were found within the insulator.

Cathodes for Combination No. 10

The cathodes (Figures 20 and 21) were more extensively damaged than the anodes. Extensive potassium interaction was found within these electrodes. The dark areas in the micrographs (A in Figures 20 and 21) are areas of extensive potassium attack. Unlike the anodes, the grain boundaries that swelled contained potassium. Little lanthanum oxide was found along these grain boundaries. Also unlike the anodes, separation was found between the nickel and the copper. Cracking occurred in the cermet.

Cathode 106. Cathode 106 (Figure 20) was examined using the SEM. In the area of maximum potassium interactions (F), the grains were smaller than in nonreactive areas, indicating a reaction that was dissolving the grains. These smaller grains of LaCrO_3 were somewhat depleted of chromium. This area of potassium attack was probably in the area where the molten seed was located during testing. The area of maximum interaction extended to the nickel-ceramic layered area of the electrode G. In the nickel-ceramic area potassium was found with the LaCrO_3 generally along the grain boundary. Potassium neither penetrated nor reacted with the nickel.

Above the reaction zone at H, the oxide second phase containing chromium and magnesium was missing. The removal of this second phase added to the porosity. This area was more porous than at I near the EPI. At I, the chromium-rich second phase was found along with LaCrO_3 and chromium-depleted LaCrO_3 . The depletion of chromium in the LaCrO_3 was more severe at the apparent EPI.

Separation of the copper and nickel was not as extensive for the cathodes as for the anodes. An example is seen in comparing J on the cathode with K on the anode. If the separation occurred during operation or cooldown, it can be concluded that the extensive potassium attack and the consequent reduction of the structural integrity of the ceramic reduced some of the residual stresses in the electrode, resulting in fewer stresses at the interface.

The insulator reacted with both the electrode and potassium. The electrode interactions occurred at the lower temperature regions, such as at L.

Some of the interaction was due to the presence of potassium. In the interaction areas, potassium was found along the insulator spinel grain boundaries. The insulator grains had some depletion of magnesium or an excess of Al_2O_3 and a considerable potassium contamination. The high alumina content in the spinel may have caused the grains to be two-phased (Al_2O_3 and MgAl_2O_4). Alumina and LaCrO_3 reacted at temperatures around 1400°K . Magnesium depletion was found near the EPI. The surface of the insulator M consisted mostly of Al_2O_3 that contained potassium and only a trace of MgO .

Electrode-Insulator Combination No. 11

Anodes 207, 208 and 209 and cathodes 107, 108 and 109 were fabricated by Westinghouse of 30 wt% 0.12 mole% Y_2O_3 -0.88 mole% ZrO_2 particles dispersed in $\text{La}(\text{MgCr})\text{O}_3$. The electrodes were made by hot pressing. The zirconia particles were about 0.5 mm/dia. The electrodes were joined to the copper cooling blocks with silver-filled epoxy. The thickness of the epoxy joint was less than 0.025 cm. The percent open porosity was the highest of all the electrodes tested in this proof test (not including the plasma-sprayed material which was not measured).

The microstructure of the untested electrode consisted of dense grains of ZrO_2 surrounded by the LaCrO_3 . The ZrO_2 grains were fractured. No LaCrO_3 penetration was found in the ZrO_2 grains. The LaCrO_3 was porous in the immediate vicinity of the ZrO_2 . No change in composition was found in the porous area; therefore, the increased porosity was probably due to incomplete sintering during hot pressing. Occasionally, metallic particles (chromium of grain size $\sim 2\text{ }\mu\text{m}$) were found in the immediate vicinity of the ZrO_2 grains.

The insulators were MgAl_2O_4 spinel. The spinel pieces were slotted at the base to help relieve stress. The insulators were joined to the copper with heat conductive silicone grease and polyimide tape.

Neither the anodes nor the cathodes remained attached to the copper block after testing. Generally, the epoxy remained attached to the copper and separated from the ceramic.

Cracks somewhat parallel to the base and located from a third of the way to half way up the base were found in both the anodes and cathodes. Some of

these cracks on the cathodes contained potassium; from this it is apparent they were present during testing. Since no phase changes in electrodes were found around the cracks, cracks were probably due to thermal stresses. In general, the cracks did not continue through the adjacent insulators.

Anodes for Combination No. 11

Anodes 207, 208 and 209 are pictured in Figures 22 and 23. A thermocouple hole (A) is shown near the copper base in Figure 22.

Anode 209. Anode 209 (Figure 23) developed two types of cracks: 1) large cracks traversing the electrode and 2) microcracks in the LaCrO_3 resulting from thermal expansion mismatches between the ZrO_2 and the LaCrO_3 . Other than the cracking, the anode's microstructure appeared unchanged between the base at A and B near the EPI. Occasional metallic chromium precipitates at the ZrO_2 grains were also found between A and B. No potassium was found in the grain boundaries. Between B and the EPI the chromium precipitates were not present. Potassium penetrated along the LaCrO_3 grain boundaries and along the interface between the ZrO_2 and the LaCrO_3 . To a depth of 0.1 mm from the EPI, the LaCrO_3 had major microstructural changes. In the restructured area two phases formed from the LaCrO_3 grains: 1) chromium-depleted LaCrO_3 and 2) La_2O_3 . The La_2O_3 was found along the grain boundaries and was probably growing into the LaCrO_3 as the chromium was depleted. In this same reaction zone some of the ZrO_2 contained lanthanum. This lanthanum diffusion into the ZrO_2 was only found at the hot surfaces near the EPI. No chromium diffusion into ZrO_2 was observed. Little potassium was found in the spinel insulators. At the plasma surface the insulator reacted with the LaCrO_3 of the anode.

Cathodes for Combination No. 11

The polished cross sections of cathodes 107, 108 and 109 are shown in Figures 23 and 24. The cathodes and insulators were more extensively damaged by potassium than were the respective anodes. The potassium attack was most severe in the central regions of the cathodes (this region was probably the temperature zone for molten salt). Like the anodes, the cathode also separated from the copper, with the epoxy generally remaining with the copper.

Cathode 109. Cathode 109 (Figure 23) was examined using the SEM EDAX. The area of extensive potassium attack (C) contained potassium on the grain boundaries. The LaCrO_3 was attacked with the dissolution of the grains. The ZrO_2 did not react with the potassium. Potassium had penetrated along the upstream edge of the cathode between the electrode and the insulator. Extensive potassium attack was found along this edge. A second phase high in chromium was found in this potassium attack area.

The major reaction zone was located between the EPI and 0.2 mm into the cathode D. Four phases were found in this area: 1) ZrO_2 with lanthanum but no potassium except at the interface between the ZrO_2 and LaCrO_3 , 2) a potassium and lanthanum oxide that contained a small amount of zirconium and aluminum, 3) LaCrO_3 with chromium depletion, and 4) MgO with some iron and LaCrO_3 . The MgO phase was an impurity phase and was found in about 5% of the surface area. The chromium-rich phase was not found in this reaction zone area, although the second phase can be found immediately below D. Less of this chromium-rich phase was found at D than C. The average size of the grains of the chromium-rich phase between C and D is about 10 μm .

The spinel insulator between E and the plasma interface contained LaCrO_3 along some of the grain boundaries. Also, the grain boundaries contained potassium. No potassium was found in the grains of the MgAl_2O_4 . Potassium was found along the grain boundaries as far as location F. The insulator crack immediately above F contained potassium, indicating the crack occurred during operation. The insulator crack immediately below E did not contain potassium and looked like a fresh fracture that probably occurred after testing.

Electrode-Insulator Combination No. 12

Anodes 210-212 and cathodes 110-112 (Figures 25 to 27) were fabricated by Westinghouse from powder prepared by General Refractories. The electrodes were brazed to nickel mesh with brazing alloy (TiCuSi). The nickel mesh was brazed to copper using Microbrazo alloy.

The insulators were monolithic MgAl_2O_4 . They were joined to the copper with a heat conductive silicone grease and polyimide tape. The insulators were slotted near the base to reduce thermal stresses.

The TiCuSi11 braze alloy wetted the electrodes, causing a bond between the nickel mesh and the electrode. Stress from differences in the coefficients of thermal expansion between the nickel and the LaCrO_3 resulted in cracking in the ceramic immediately above the bonding (see A in Figure 25 for an example). The cracks were found where the cross-sectional length of bonding exceeded 0.08 mm.

Anodes for Combination No. 12

The anodes were less damaged than the cathodes. The surface of the anodes appeared to be more uniformly eroded than the roughened surfaces of the cathodes. Potassium penetrated the anodes less than it did the cathodes. The anodes were less severely cracked than were the cathodes.

Anode 212. Anode 212 (Figure 26) is typical of anodes 210 and 211. The reaction zone (A) extends only to a depth of 0.6 mm from the EPI. From the EPI to a depth of 0.05 mm the material comprised two phases. Both of the phases contained mostly lanthanum oxide with small quantities of either CaO-stabilized ZrO_2 or SiO_2 . Between 0.05 mm and 0.1 mm the anode was two-phased: 1) La(Mg)CrO_3 with some chromium depletion and 2) chromium oxide with a small amount of MgO. Between 0.1 mm and 0.6 mm a third phase was found along the grain boundaries. This third phase contained lanthanum oxide with some silica.

The remainder of the microstructure between A and B was similar to the original microstructure, containing two phases: 1) LaCrO_3 with small amounts of MgO and 2) Cr_2O_3 with MgO and some La_2O_3 (5% of area). The pores were irregularly shaped and were located mostly along grain boundaries. Potassium was generally not found in anode 212. The potassium reaction at C was due to migration of potassium along the separation between the electrode and the downstream channel exit section. Migration of potassium also occurred between the upstream electrode and insulator.

The upstream insulator reacted with anode 212 at the hot regions. Lanthanum oxide was found as a second phase intermixed with the spinel near the insulator surface D. The lanthanum migrated into the spinel. No spinel was found in the anode.

Cathodes for Combination No. 12

The EPI of the cathodes showed much more damage than the respective anodes. Part of this observable damage of the surface shown on the micrograph is due to hydration effects. The hydration is due to greater concentrations of potassium in the cathode EPI than the anode.

Cathode 112. In cathode 112 (Figure 26) the reaction zone extended much farther into the electrode than was the case for the respective anode. The reaction zone (E) extends to a depth of 7.3 mm. The potassium penetration and interaction was much more extensive on the cathode than on the anode. The potassium interaction generally defines the reaction zone.

At the EPI F, cathode 112 is two-phased: 1) chromium-depleted LaCrO_3 (90% of area) and 2) lanthanum oxide at the grain boundaries. Immediately below the EPI at G, the material was three-phased: 1) LaCrO_3 slightly depleted in chromium (60% of area), 2) lanthanum oxide with some silicon and potassium (30% of area), and 3) LaCrO_3 slightly depleted in chromium and containing potassium. The third phase was granular and intermixed with the first phase. Lanthanum oxide was found as a second phase in between G and H. The demarcation at H represents the transition to La_2O_3 -free areas. Between H and E no La_2O_3 was found along the grain boundaries or in the grains. The high-chromium second phase found in the untested specimens was not found in this area. The porosity in this phase increased, compared to the area between E and the base of the cathode. The increase in porosity seemed to be due to the leaching of the second phase because of potassium attack. Below E the microstructure resembled that found in the untested material. Potassium was found only in the area above E.

The large horizontal crack below R occurred after the test. The cracking may have resulted from the swelling caused by potassium hydration at I.

Potassium was found in the spinel insulator between the plasma-insulator interface J. Potassium was found along the grain boundaries. The grain boundaries were enlarged in this area, indicating potassium attack.

PROOF TEST NO. 3

The third proof test was conducted January 4-5, 1978. The test consisted of four phases: 1) startup and heatup of channel, 2) calibration tests to compare diagnostics and check thermocouples, 3) steady-state operation with potassium seed, and 4) cooldown and shutdown of channel. Data concerning the electrodes and insulators for this proof test are summarized in Table 3. The measured densities were for the ceramic portion of the electrode and did not include any metal mesh current leadout.

The electrodes and insulators were run for 21.8 hr in an electric field; the plasma used was seeded with potassium. All but three electrode pairs had a current flow of 1 A/cm². The three electrode pairs with reduced current flow were 101 and 201 (0.12 A/cm²), 102 and 202 (0.24 A/cm²) and 112 and 212 (0.36 A/cm²). Although the external circuitry measured the appropriate current flows, no internal checks were maintained to insure that the current went through the plasma instead of short circuiting through the insulating sidewalls. Posttest disassembly of the channel showed massive seed penetration of the sidewalls. The seed was moist near the cooler areas (water vapor condensation points) and could have conducted electrical current. The sidewalls in this test contained more seed than the sidewalls in either test 1 or 2. Three electrode pairs (103 and 203, 107 and 207, and 108 and 208) required much less electrical potential to achieve the experimental current densities than the other electrodes, indicating that at least these three electrodes had some sorting through the insulator wall. Westinghouse will conduct detailed analyses of the electrical and thermal characteristics of this test.

After testing, Westinghouse cut the cathode wall in half using a diamond saw and water as the coolant. The sample was severely cracked, partly because of the sawing. Moisture from cutting caused some disruption of the cathodes because of potassium hydration. At PNL, half the cathode wall was cut parallel to the Westinghouse cut at 0.9 cm from the cut. A SiC saw blade with kerosene coolant was used to make the cut. Damage from the Westinghouse cut was found in this location; therefore, a second cut was made 0.6 cm and parallel to the first cut. In this location the initial cutting cracks were not so prevalent; consequently, the surface exposed by the second cut was examined

TABLE 3. Electrodes and Insulators for Proof Test No. 3

Electrode Insulator Combination	Channel Location	Material	Source	Fabricator	Fabrication Technique	Density g/cm ³ (% TD)	Porosity			Attachment Method
							% Total	% Closed	% Open	
13 Electrode	101-103 and 201-203	La _{0.95} Mg _{0.05} Al _{0.32} Cr _{0.68} O ₃ La _{0.95} Mg _{0.05} Al _{0.24} Cr _{0.76} O ₃ + La _{0.95} Mg _{0.05} Al _{0.15} Cr _{0.85} O ₃	AT Research	Westinghouse	Hot-pressed at 1893°K and 1.37x10 Pa	6.3 (95.4)	4.6	3.9	0.7	Silver-gold film to copper
Insulator		MgO	Norton	Norton	Hot-pressed					
14 Electrode	104-106 and 204-206	0.5La _{0.95} Mg _{0.05} CrO ₃ -0.5 SrZrO ₃	AT Research	AT Research	Sintered	5.3 (89)	11.0	3.1	7.9	Silver epoxy platinum film to copper
		MgO	Trans Tech	Trans Tech	Sintered					
15 Electrode	107-109 and 207-209	LaCrO ₃	General Electric	General Electric	Sintered	3.6 (89.6)	10.4			Flexbed to soldered copper
Insulator		MgAl ₂ O ₄	General Electric	General Electric	Sintered					
16 Electrode	110-112 and 210-212	0.25Fe ₃ O ₄ -0.75MgAl ₂ O ₄ + "hercynite"	Trans Tech	APS Materials	Plasma- sprayed	5.98 (90)	10			Hercynite plasma sprayed on nickel-plated copper
Insulator		MgAl ₂ O ₄	Trans Tech	APS Materials	Plasma- sprayed					

metallographically. Several of the cathodes were not polished for metallographic examination because of excessive microstructural damage, which might have been caused by potassium hydration.

Westinghouse also cut the anode in half. This cut was not so damaging as the cut on the cathode. The surface exposed by the Westinghouse cut was examined metallographically.

The unpolished metallographic surfaces of both anode and cathode walls are shown in Figure 28. The extensive bloating of the cathode is shown at A, where some of the cathode was entrapped in the Maraset mounting medium above the bulk area of the electrode. The direction of plasma flow is shown by the arrow.

For this test, only electrodes 103 and 203 were examined in detail. The other electrode configurations did not perform as well as other tested configurations and, thus, will not be used in the U-02 Phase III Test. Consequently, analysis of these configurations was not conducted as part of the program to choose electrodes and insulators for the U-02 tests. The polished sections are shown in this report, but detailed description of the microstructural changes are not included.

In general, potassium attack (or at least erosion and corrosion) was more extensive in the anode than in the cathode. Anodes 204-206 were the most severely eroded. These anodes were more severely eroded than the adjacent insulators, resulting in a hill/valley topography. The next most severely damaged anodes were anodes 207-209, whose insulators were more eroded than the anodes themselves. With these anodes, the current transfer between the plasma and electrode tended to bypass the electrode and go directly to the flexbed leadout. Apparently this current bypassing eroded these insulators. Anodes 210-212 and 201-203 were more uniformly eroded except for anode 203, which eroded excessively because of the erosion of anode 204.

The most severely damaged cathodes were cathodes 104-106. These electrodes were more uniformly eroded than the respective anodes. For cathodes 104 and 105, some electrode material flowed over the insulators. Cathodes 110-112 were the second most severely damaged cathodes. The samples

bloated, with the bloating most severe at the edges of the electrode in contact with the simulator sidewall. The major bloating was in the hercynite layer (see B in Figure 28). This layer was reddish in color, indicating Fe_2O_3 . The bloating resulted in separation of the MAFF from the hercynite. The third most damaged cathodes were cathodes 107-109. Some of the surface layers spalled during the posttest visual examination. The erosion, seen on the insulators between the electrodes, was not found on these cathodes. The least eroded cathodes were cathodes 101-103. These cathodes had the reddish appearance of a lanthanum aluminate. Interaction was found between the electrode and insulator. This interaction resulted in a yellowish coloration of the insulator.

Electrode-Insulator Combination No. 13

Anodes 201-203 and cathodes 101-103 were fabricated by Westinghouse from alumina-enriched lanthanum chromite. In this material aluminum replaced the chromium. The electrodes were layered, with the greatest amount of alumina substitution at the EPI.

The composition near the EPI ($\text{La}_{0.95}\text{Mg}_{0.05}\text{Al}_{0.32}\text{Cr}_{0.68}\text{O}_3$) consisted of three phases. The first phase was LaCrO_3 with some chromium depletion. It existed as islands surrounded by a two-phased material. These two phases were an intermixed structure of: 1) LaCrO_3 with increased chromium and containing aluminum and magnesium, and 2) LaCrO_3 with some chromium depletion and containing aluminum in lesser quantity than the previous phase. No MgO was found in this second phase (1 mole% is the minimum detection limit).

The area between the EPI and the bulk of each electrode ($\text{La}_{0.95}\text{Mg}_{0.05}\text{Al}_{0.24}\text{Cr}_{0.76}\text{O}_3$) had a microstructure similar to the phase near the EPI except that the overall aluminum content was lower. This phase was less porous than the composition near the EPI.

The rest of each electrode was made up of a third composition, $\text{La}_{0.95}\text{Mg}_{0.05}\text{Al}_{0.15}\text{Cr}_{0.85}\text{O}_3$. This composition had two phases: 1) LaCrO_3 and 2) an oxide containing magnesium and aluminum with small amounts of lanthanum and cerium. Apparently, most of the additional magnesium and aluminum was found as a second phase and was not in the LaCrO_3 matrix. Because of the phase

separation and the concentration of the additions in the second phase, it is not known how effective these additions were in modifying the properties of the LaCrO_3 .

Anodes for Combination No. 13

Figures 29, 30 and 31 show the three anodes. The reaction zone is clearly defined in A in Figure 29. The reaction zone was severely cracked with some potassium penetration along the cracks. Below the reaction zone B the microstructure remained unaltered. A similar reaction zone was found in Anode 202 (A in Figure 30). Severe cracking was also found in this zone. The cracking in anode 201 and 202 was not found in anode 203 (Figure 31). In this anode, the reaction zone was affected by anode 204; SrZrO_3 had migrated into the reaction zone, resulting in enhanced corrosion.

A thermocouple at B in Figure 30 is type K used in the test to monitor the temperature of the cold center area of the insulator. The thermocouple gave readings throughout the test, although near the end of the test the values were somewhat erratic. No evidence was seen of potassium migration into the thermocouple area or of interaction between the thermocouple sheath and the anode. At least in the area exposed by polishing, the sheath chemically isolated the insulator from the anodes. For all three anodes the epoxy attachment degraded and each of them separated from the copper. Although some epoxy remained with the anodes, most of the epoxy remained on the copper.

Anode 203. Anode 203 (Figure 31) was much more degraded than were anodes 201 and 202. Part of this degradation was due to the severe erosion of anode 204, which exposed the area of anode 203 that operates at temperatures where seed would be mostly in the liquid state. Consequently, the central portion of anode 203 (See B in Figure 31) was severely attacked by potassium. In this reaction area, the major phases were: 1) potassium and 2) lanthanum oxide with a small amount of chromium.

Above the reaction zone at C the microstructure appeared as particles separated by enlarged grain boundaries. The grain boundaries were filled with potassium. LaCrO_3 was depleted in chromium; no chromium-rich second phase was found. The oxide phase containing magnesium and aluminum also was absent.

At D the microstructure consisted of LaCrO_3 that was slightly depleted in chromium. The magnesium- and aluminum-containing second phase in the untested material was absent. Both potassium and aluminum were found at the grain boundaries. Areas of high chromium concentration were also found at the grain boundaries.

Two phases were found at E: 1) LaCrO_3 with some aluminum and a slight depletion of chromium (no potassium was found) and 2) LaCrO_3 containing some potassium and with a higher aluminum concentration than the first phase. Two phases were found at the EPI at F: 1) La_2O_3 and 2) LaCrO_3 that was depleted of most of the chromium. The aluminum content of the LaCrO_3 phase was higher than that initially present.

At A, the major contaminants of the chromium-depleted LaCrO_3 were SrZrO_3 and MgAl_2O_4 . These contaminants were found along the surfaces of the reaction zone. The surfaces of the insulator did not have any SrZrO_3 deposits.

Large cracks were found in the electrode below the reaction zone. The cracks at G and H contained potassium, indicating the cracks formed during operation.

The upstream MgO insulator reacted with potassium. The insulator was initially fine-grained (25 grain size) with porosity along the grain boundaries. The grain boundaries contained silicon as the major impurity. Potassium migrated along the grain boundaries, as did some LaCrO_3 from the electrode. The potassium attacked the grain boundaries.

Cathodes for Combination No. 13

The cathodes are shown in Figures 29, 30 and 31. The reaction zone is shown at I in each of the figures. The reaction zone is about equal for all three cathodes, even though cathode 103 operated at a higher current density. Although not enriched with aluminum to the same degree, chromites from proof tests 1 and 2 showed effects of electric current. Several explanations for the apparent independence of the reaction zone to the current density are: 1) the reactions are related to the higher alumina contents and occur in these areas, 2) the reactions are solely temperature-dependent and follow outlines of temperature zones, 3) the electrochemical reactions are masked by other

corrosion mechanisms, and 4) current transport is not through the plasma but shorts between the anode and cathode through the insulator walls. It has not been possible to determine the mechanism that produced the uniform corrosion.

The attachment of the cathode to the copper failed for cathodes 101 and 102. Unlike the anodes, all the epoxy remained with the copper. Cathode 103 remained attached to the copper. No evidence was found of debonding along the epoxy interface to cathode 103.

Cathode 103. Cathode 103 (Figure 31) showed few microstructural changes up to the reaction zone. Potassium did not penetrate the cathode except in the reaction zone. An area of high potassium concentration is shown at J in Figure 31. In this potassium-rich area the matrix grains are highly depleted in chromium and aluminum. At the EPI (K), the chromites were highly depleted in chromium. The grains contained aluminum. The magnesium-aluminum second phase was missing.

A detailed analysis of the reaction zone at L showed that the cathode began to break up as potassium penetrated the porous LaCrO_3 that contained the greater amounts of aluminum. Some of the alumina may have concentrated on the boundary, thereby enhancing potassium penetration. Three phases were initially present in this area: 1) LaCrO_3 with high aluminum concentrations and with a porous morphology, 2) LaCrO_3 with a high chromium content and with an aluminum content lower than phase 1, and 3) small precipitates of magnesium, aluminum and some chromium. Phases 2 and 3 were intermixed and appeared as dense islands surrounded by phase 1. After penetrating the porous phase 1 and interacting with the grains, the potassium began to penetrate along the fine porosity in the islands of phases 2 and 3. Potassium then interacted with phase 3 (the oxide containing magnesium and aluminum and chromium) and removed this phase, leaving a porous structure of phase 2. The resulting microstructure was porous with potassium and other impurities at the grain boundaries; this was the same microstructure seen in the reaction zone. The reaction sequence leading to degradation may have been altered by reducing the porosity of phase 1 and removing the magnesium-, aluminum-, and chromium-rich third phase.

Electrode-Insulator Combination No. 14

Anodes 204-206 and cathodes 104-106 were fabricated by A.T. Research of $0.5\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3-0.5\text{SrZrO}_3$. This material contained two phases. The electrodes were porous with 7.9% open, interconnected porosity. The non-spherical porosity occurred along grain boundaries and may have been 5-6 μ m wide. Capillarity can occur with these sizes of pores. A microstructure with porosity of this morphology aids in seed penetration and greatly increases the surfaces available for seed-electrode interaction.

Anodes for Combination No. 14

The anodes are shown in Figures 32 and 33. Potassium is found throughout the anodes. The large amount of potassium in the anodes was due to the open porosity and may have been enhanced by capillary forces. The mid-temperature zone of the anodes at A in Figure 32 and 33 had the greatest amount of potassium concentration. The most potassium penetration and interaction was found in anode 204. The potassium attack in this anode enlarged the grain boundaries.

All three anodes changed microstructurally near the EPI, as shown at B in Figures 32 and 33. These microstructural changes included a change in composition as evidenced by the color change from a dark brown-black to a purplish gray, and by a densification of the material. The EPI was two-phased, with SrZrO_3 separating from the LaCrO_3 . Anode 204 also densified near the copper leadout (see C in Figure 32). This densification was due to localized heating from current transport between the anode and the copper. The anode separated from the copper. Electrical contact was maintained with the copper near C. The same effect is seen at C in Figure 33. The localized heating in this anode caused some material loss on the copper.

The microstructural changes at the EPI indicated that anode 204 was running at temperatures that were too high. Poor thermal transport across the separation between the anode from the copper may have been the cause of the excessive temperatures at the EPI. Finding the areas of current transport between the electrode and copper for anodes 204 and 206 verified that a separation did, in fact, occur during channel operation, and not upon cooldown or sample preparation prior to mounting in Maraset.

The anodes interacted with the insulators at the hot temperature regions. The insulator damage associated with the change in composition of the electrode at high temperatures for this interaction was not observed in the respective cathodes.

Cathodes for Combination No. 14

The cathodes were severely damaged, partially from exposure to moisture during the initial cutting and the consequent hydration of potassium and lanthanum compounds. Only the least damaged cathode is shown in Figure 33. Although this electrode separated from the copper, it is not known if the separation occurred during the test. The cathode overheated during operation and formed a restructured zone of dense, two-phased material. Some of the dense grains can be seen at E.

Potassium penetrated the sample and concentrated at mid-temperature regions, such as F. In these areas, the grain boundaries were enlarged by potassium attack. Potassium was found in the porosity throughout the cathode--even at the base near the copper. Potassium was also found in the MgAl_2O_4 . Potassium migrated into the spinel from the interfaces between the insulator and electrode. The reaction associated with this migration zone is shown at G.

The cathodes reacted with the insulators much less than did the respective anodes. Other than some interaction at the electrode-insulator interface, the cathode we examined was to have penetrated the electrode very little.

Electrode-Insulator Combination No. 15

Anodes 207-209 and cathodes 107-109 were fabricated by General Electric of doped lanthanum chromite. The anodes are shown in Figures 34 and 35. In all three anodes and in the cathode (Figure 35) cracks developed along the attachment area near the tips of the metallic fingers protruding into the samples at A in the respective figures. These cracks could result in the loss of the electrode if the electrodes were not held in place by the insulator side-walls.

Potassium was not found in the LaCrO_3 except at the edges, interfaces, and cracks. In these areas, the potassium penetrated along grain boundaries and enlarged these boundaries through chemical interactions.

Questions were raised during the analysis of the electrical data as to whether the electric current bypassed part of the ceramic and went directly to the metallic flexbed. No other evidence was found to collaborate or refute the questions. For this reason, the stability of these electrode materials in the presence of electric current may not be determinable from these proof tests.

Figure 35 shows one of the cathodes for this electrode-insulator combination. The others sustained water damage after initial cutting. The cathode pictured in the micrograph showed some potassium penetration. More of the cathode remained immediately after the test but was lost due to hydration. Potassium hydration was the major cause of damage. Potassium interacted with the grains to the extent that the average grain size in the reaction zones was nearly half that of the grains in the nonreaction zones. Potassium was also found in the flexbed but did not react with the metal in the flexbed.

Electrode-Insulator Combination No. 16

Anodes 210-212 and cathodes 110-112 were fabricated at APS by plasma-spraying a series of compositions on a copper block that had been ion-plated with a coating of nickel. The base layer consisted of approximately 3 mm of a hercynite METCO 447 composite (METCO Incorporated, New York): The intermediate was hercynite (Fe_3O_4 doped) and the outer layer was MAFF-31 ($0.75 \text{ MgAl}_2\text{O}_4 \cdot 0.25 \text{ Fe}_3\text{O}_4$, Trans Tech Inc.). The polished microstructure showed the plasma-sprayed layers as they were deposited on the electrodes. Both the electrodes and insulators contained unevenly distributed, irregularly shaped porosity. Areas of the sample show interconnected clusters of pores. The electrodes were in contact with the copper. The hercynite/METCO 447 composite did not separate from the copper. The electrodes, both anodes and cathodes, cracked severely within the hercynite. Some of this cracking occurred during channel disassembly and cutting after cooldown. Overall, the anodes were less damaged and eroded than the cathodes.

Anodes for Combination No. 16

Anodes 210-212 (Figures 36 and 37) eroded uniformly. The EPI showed microstructural changes, but not the gross changes caused by operating at too high a temperature. The polished surfaces looked as though the EPI had spalled, leaving an essentially unreacted surface. No spalled material was found in the channel upon disassembly. Of course, spalling during initial stages of cooldown would be swept out of the channel by the plasma.

Each of the anodes was severely cracked in the hercynite area. All the cracks appeared at the same general location--in the hercynite, approximately 1 mm below the spinel-hercynite interface. The hercynite has less mechanical strength than the MAFF-31. Using a metallic probe, the hercynite could be removed from the surface more easily than could the MAFF-31.

Cathodes for Combination No. 16

Only the microstructure of cathode 112 (Figure 37) is shown. All the cathodes were severely damaged by hydration. Some of the swelling occurred during the posttest observation period prior to mounting in Maraset. The swelling mainly occurred in the hercynite. The hercynite was reddish brown in color and contained green flecks (hydrated potassium compound). The dark area at A in Figure 27 shows the hercynite-hydration zone. The material was too soft and poorly bonded to polish. The hydrated hercynite was so poorly bonded it easily crumbled between the fingers. Potassium had leaked from the electrode during storage. Although the hercynite addition appeared to form a good bond with the METCO 447 and the nickel-plated copper, it did not show the resistance to potassium attack nor maintain sufficient structural integrity to be used as an intermediary layer for clean-fired MHD channel conditions.

112 111 110 109 108 107 106 105 104 103 102 101

CATHODE

10 mm

201 202 203 204 205 206 207 208 209 210 211 212

ANODE

FIGURE 1. Unpolished Metallographic Surfaces of Anodes and Cathodes from Proof Test No. 1

FIGURE 2. Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ Anode and Cathode at Locations 201 and 101, Proof Test No. 1

FIGURE 3. Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ Anode and Cathode at Locations 211 and 111, Proof Test No. 1

FIGURE 4. Microstructure of $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ Anode and Cathode at Locations 212 and 112, Proof Test No. 1

FIGURE 5. Microstructure of $x\text{Fe}_3\text{O}_4-(1-x)\text{MgAl}_2\text{O}_4$ Anode and Cathode at Locations 202 and 102, Proof Test No. 1

FIGURE 6. Microstructure of $x\text{Fe}_3\text{O}_4-(1-x)\text{MgAl}_2\text{O}_4$ Anode and Cathode at Locations 203 and 103, Proof Test No. 1

FIGURE 7. Microstructure of $x\text{Fe}_3\text{O}_4-(1-x)\text{MgAl}_2\text{O}_4$ Anode and Cathode at Locations 204 and 104, Proof Test No. 1

FIGURE 8. Microstructure of $0.25\text{Fe}_3\text{O}_4\text{-}0.75\text{MgAl}_2\text{O}_4$ Anodes at Locations 205-207, Proof Test No. 1

FIGURE 9. Microstructure of $0.25\text{Fe}_3\text{O}_4\text{-}0.75\text{MgAl}_2\text{O}_4$ Cathodes at Locations 105 and 106, Proof Test No. 1

FIGURE 10. Microstructure of $0.25\text{Fe}_3\text{O}_4\text{-}0.75\text{MgAl}_2\text{O}_4$ Cathode at Location 107, Proof Test No. 1

FIGURE 11. Microstructure of Hafnia-Based Anode and Cathode at Locations 208 and 108, Proof Test No. 1

FIGURE 12. Microstructure of Hafnia-Based Anode and Cathode at Locations 209 and 109, Proof Test No. 1

FIGURE 13. Microstructure of Hafnia-Based Anode and Cathode at Locations 210 and 110, Proof Test No. 1

201 202 203 204 205 206 207 208 209 210 211 212

ANODE

10 mm

101 102 103 104 105 106 107 108 109 110 111 112

CATHODE

FIGURE 14. Unpolished Metallographic Surfaces of Anodes and Cathodes from Proof Test No. 2

FIGURE 15. Microstructure of Hot-Pressed Graded LaCrO₃-ZrO₂ Anodes at Locations 201 and 202, Proof Test No. 2

FIGURE 16. Microstructure of Hot-Pressed Graded $\text{LaCrO}_3\text{-ZrO}_2$ Anode at Location 203, Proof Test No. 2

FIGURE 17. Microstructure of Hot-Pressed Graded $\text{LaCrO}_3\text{-ZrO}_2$ Cathodes at Locations 101 and 102, Proof Test No. 2

FIGURE 18. Microstructure of Hot-Pressed Graded $\text{LaCrO}_3\text{-ZrO}_2$ Cathode at Location 103, Proof Test No. 2

FIGURE 19. Microstructure of Plasma-Sprayed Graded $\text{LaCrO}_3\text{-ZrO}_2$ Anodes at Locations 204 and 205, Proof Test No. 2

FIGURE 20. Microstructure of Plasma-Sprayed Graded $\text{LaCrO}_3\text{-ZrO}_2$
Anode and Cathode at Locations 206 and 106, Proof Test No. 2

FIGURE 21. Microstructure of Plasma-Sprayed Graded $\text{LaCrO}_3\text{-ZrO}_2$ Cathodes at Locations 104 and 105, Proof Test No. 2

FIGURE 22. Microstructure of Hot-Pressed $\text{LaCrO}_3\text{-ZrO}_2$ Anodes at Locations 207 and 208, Proof Test No. 2

FIGURE 23. Microstructure of Hot-Pressed $\text{LaCrO}_3\text{-ZrO}_2$ Anode and Cathode at Locations 209 and 109, Proof Test No. 2

FIGURE 24. Microstructure of Hot-Pressed $\text{LaCrO}_3\text{-ZrO}_2$ Cathodes at Locations 107 and 108, Proof Test No. 2

FIGURE 25. Microstructure of LaCrO₃ Anodes at Locations 210 and 211, Proof Test No. 2

FIGURE 26. Microstructure of LaCrO_3 Anode and Cathode at Locations 212 and 112, Proof Test No. 2

FIGURE 27. Microstructure of LaCrO₃ Cathodes at Locations 110 and 111, Proof Test No. 2

FIGURE 28. Unpolished Metallographic Surfaces of Anodes and Cathodes from Proof Test No. 3

FIGURE 29. Microstructure of Alumina-Doped LaCrO_3 Anode and Cathode at Locations 201 and 102, Proof Test No. 3

FIGURE 30. Microstructure of Alumina-Doped LaCrO_3 Anode and Cathode at Locations 202 and 102, Proof Test No. 3

FIGURE 31. Microstructure of Alumina-Doped LaCrO_3 Anode and Cathode at Locations 203 and 103, Proof Test No. 3

FIGURE 32. Microstructure of $0.5\text{SrZrO}_3\text{-}0.5\text{LaCrO}_3$ Anodes at Locations 204 and 205, Proof Test No. 3

FIGURE 33. Microstructure of $0.5\text{SrZrO}_3\text{-}0.5\text{LaCrO}_3$ Anode and Cathode at Locations 206 and 106, Proof Test No. 3

FIGURE 34. Microstructure of LaCrO₃-Flexbed Anodes at Locations 207 and 208, Proof Test No. 3

FIGURE 35. Microstructure of LaCrO_3 -Flexbed Anode and Cathode at Locations 209 and 109, Proof Test No. 3

FIGURE 36. Microstructure of MAFF-31/Hercynite Anodes at Locations 210 and 211, Proof Test No. 3

FIGURE 37. Microstructure of MAFF-31/Hercynite Anode and Cathode at Locations 212 and 112, Proof Test No. 3

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