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MASTER

RARE-EARTH HAFNIUM OXIDE MATERIALS FOR MAGNETOHYDRODYNAMIC (MHD) GENERATOR APPLICATION

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Several ceramic materials based on rare-earth hafnium oxides have been identified as potential high-temperature electrodes and low-temperature current leadouts for open cycle coal-fired MHD generator channels. The electrode-current leadouts combination must operate at temperatures between 400 and 2000K with an electrical conductivity greater than 10^{-2}ohm^{-1}cm^{-1}. The electrodes will be exposed to flowing (linear flow rates up to 100 m/s) potassium seeded coal combustion gases (plasma core temperatures between 2400-3200K) and coal slag. During operation the electrodes must conduct direct electric current at densities near 1.5 amp/cm^2. Consequently, the electrodes must be resistant to electrochemical decompositions and interactions with both the coal slag and potassium salts (e.g., K_2SO_4, K_2CO_3). The current leadout materials are placed between the hot electrodes and the water-cooled copper structural members and must have electrical conductivities greater than 10^{-2}ohm^{-1}cm^{-1} between 1400 and 400K. The current leadouts must be thermally and electrochemically compatible with the electrode, copper, and potassium salts. Ideally, the electrodes and current leadouts should exhibit minimal ionic conductivity.

Several materials have been suggested as possible candidates for electrodes. These include doped lanthanum chromites (1,2), iron doped magnesium alumina spinel (1,2), stabilized zirconia (1,2), doped yttrium chromites (3), and rare-earth hafnium oxides (4,5). This paper focuses on rare-earth hafnium oxides.

Several rare-earth hafnium oxides have adequate electrical conductivity at temperatures above 1100K; however, at lower temperature the conductivity is not adequate for direct contact with the copper. Consequently, current leadout materials are needed. Several

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rare-earth hafnium oxide M_xO_y ceramics (M_xO_y represents a highly conductive oxide) have been developed which have adequate electrical conductivity and are thermally and electrochemically compatible with the rare-earth hafnium oxide electrodes (3).

Fabrication

Sinterable hafnium oxide rare-earth oxide powders (BET surface areas around 14 m^2/g) were coprecipitated from neutralized dilute acidic solutions of the cations using a process similar to that of Dole, et al. (6). The acidic solutions were made from dissolving the rare-earth oxides in concentrated boiling HCl or HNO_3 and the hafnium oxychloride in water. Neutralized to a pH of 7.5 with dilute NH_4OH, the precipitate was washed with acetone and toluene, dried and air calcined for 2-4 hrs between 1100-1300K. The powders were ground through -200 mesh or ball milled with steel balls for 6-8 hrs, then cold die pressed at 82.7 MPa and isostatically pressed at 154 MPa and sintered in vacuum between 2173 and 2273K for as-ground powders or 1900-2100K for the ball milled powders. The sintered samples were partially reduced (dark blackish color) and were reoxidized (buff color) by air at 1773K.

The limited equilibrium phase data for Re_2O_3-HfO_2 appears similar to the better known analogous $Re_2O_3 \cdot ZrO_2$ systems. When added to HfO_2, the larger rare earth cations tend to form pyrochlore structures (7,8) and the smaller cations tend to form fluorite solid solutions (7,9). The predicted crystallographic structures of the rare earth cations were obtained after heat treatment. For most of the compositions, the predicted structures developed after the low temperature calcine.

Electrical Conductivity

The DC electrical conductivity using a 4 probe technique was measured in air to 1620K for several of the compositions. The range of values are shown in Figure 1 along with data for other potential electrode materials. Included in the Figure is data for the current lead out and undoped HfO_2 (12). The electrical conductivity of the current lead out materials are between 10^{-1} and $10^{-2} ohm^{-1} cm^{-1}$ at 300K. Of the electrode compositions, the highest electrical conductivity are those with the fluorite phase containing less than 30 mol% Re_2O_3. The results are consistant with data on Er_2O_3-HfO_2 (10) and Y_2O_3-HfO_2 (11).

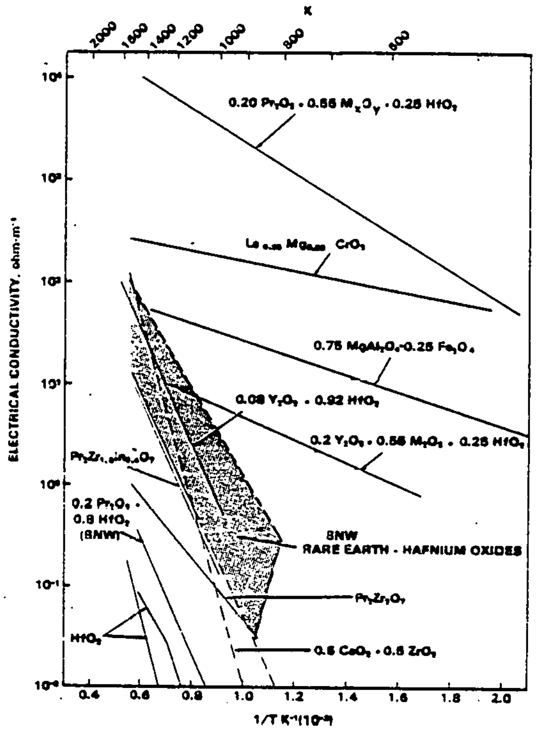

Figure 1. Electrical conductivities of rare-earth hafnium oxides compared with other hafnates, zirconates and some potential MHD electrodes.

Electrochemical Corrosion

The electrochemical corrosion of several rare-earth hafnium oxides was measured in molten coal slag/alkali seed using laboratory test methods (4). An anode and cathode were suspended in the molten slag/seed electrolyte and a direct current passed between these electrodes. Aluminum oxide sleeves were placed around the electrodes to direct the current through the ends of the electrodes. A platinum voltage probe equidistant from each electrode measured the electric potential of the anode and cathode. Tests were conducted in molten K_2SO_4 (at 1373K) and synthetic Montana "Rosebud" (MR-1) coal slag (at 1720-1730K) containing K_2O. The composition of the MR-1 was 42.4% (weight percent) SiO_2, 18.8% Al_2O_3, 12.9% CaO, 6.9% Fe_2O_3, 4.1% MgO, 0.7% TiO_2, 13.4% K_2O, 0.4% Na_2O, and 0.2% P_2O_5.

The corrosion rates were determined by geometry changes and material loss measured after metallographic preparation. These enhanced rates provided a relative corrosion resistance for comparing different materials but cannot be related directly to corrosion rates anticipated in an MHD channel.

The electrochemical corrosion rates of the rare-earth hafnium oxides are listed in Table 1. Comparative corrosion rates in molten MR-1 coal for lanthanum chromites, yttrium chromites, and iron containing magnesium aluminate spinel varied between 30-280 µg/coul, 13-160 µg/coul and 140-470 µg/coul, respectively. In contrast, the better hafnia-base compositions exhibited corrosion rates $\leq$10 µg/coul.

The corrosion of the rare-earth hafnium oxides in molten K_2SO_4 were much less than in the molten coal slags, Table 1. Little potassium penetration occurred in either anode or cathode. For comparison, the electrochemical corrosion rates in K_2SO_4 tested under similar conditions for the lanthanum chromite, yttrium chromite and iron doped magnesium aluminate spinels were 45-500 µg/coul, 5-30 µg/coul and 60-140 µg/coul, respectively.

The corrosion processes for the rare-earth hafnium oxides were very similar, with the rates varying with the rare earth additions. In a typical test (Test 163: $Yb_{0.64}Hf_{0.36}O_2$ in MR-1 slag), slag interacts with the grain boundaries of the cathode causing grain separation. Continued reaction results in grain loss into the slag. The reaction products of the slag/seed-hafnia interaction consists of $K_{0.15}Si_{0.32}Al_{0.03}Yb_{0.13}O_{2+x}$ and $Ca_{0.16}Si_{0.17}Al_{0.16}Yb_{0.38}O_{2+x}$.* The Yb was selectively removed from the matrix grains, ultimately leaving a $Yb_{0.41}Hf_{0.59}O_2$ composition, probably a fluorite phase. No other products were observed, except for some metallic iron in the slag near the cathode surface, probably resulting from the charge transfer reaction between the cathode and the slag.

Table 1. Electrochemical Corrosion of Several
Rare-Earth Hafnia Compositions

Composition	Electrolyte	Current Density, A/cm^2	Corrosion Rate, µg/coul Anode	Corrosion Rate, µg/coul Cathode
$Tb_{0.31}Hf_{0.69}O_2$	K_2SO_4	1.6	1-5	1-5
$Tb_{0.31}Hf_{0.69}O_2$	MR-1	1.6	3	5
$Pr_{0.04}Yb_{0.08}Tb_{0.17}Hf_{0.71}O_2$	K_2SO_4	0.5-1	1-5	1-5
$Pr_{0.04}Yb_{0.08}Tb_{0.17}Hf_{0.71}O_2$	MR-1	0.8	5-10	3-6
$Yb_{0.09}Pr_{0.27}Hf_{0.64}O_2$	MR-1	1	11	43
$Pr_{0.04}Yb_{0.08}Tb_{0.17}Hf_{0.71}O_2$	MR-1	0.7-1.2	12	16
$Tb_{0.31}Hf_{0.69}O_2$	MR-1	1 0.5	50-82	25-53
$Yb_{0.64}Hf_{0.36}O_2$	MR-1	1.2	55	99
$Tb_{0.18}Hf_{0.82}O_2$	MR-1	1.2	3-6	--
$Pr_{0.2}Hf_{0.8}O_2$	K_2SO_4	0.3	12-24	12-24
$Tb_{0.18}Hf_{0.82}O_2$	MR-1	1.1	16-32	126
$Eu_{0.06}Sm_{0.11}Hf_{0.83}O_2$	MR-1	1	5-14	200-400

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*The compositions determined by quantitative scanning electron microscopy and microprobe (SEM-EDX). The oxygen analysis is an estimate since oxygen cannot be detected directly.

The electrochemical processes appear strongly dependent upon the electrochemical and electrical character of the slag/seed electrolyte, e.g., the ionic and electronical transport. Paggage of a dc current through the molten electrolytes results in ionic migration toward the anode and cathode. In molten potassium salts, K^+ migrates toward the cathode and $CO_3^=$ or $SO_4^=$ migrates to the anode. In complex coal slag/seed, the specific migrating ions, the degree of slag ionicity and the electronic-ionic transfer mechanism across the slag-oxide interfaces are not known. It is assumed that cations (K^+,Ca^{++}, Na^+) in coal slag carry a majority portion of the current in the "Rosebud" slag. The anion transfer between the anode and slag is more complex and could involve the decomposition of silicate ion ($SiO_4^=$) and the formation of O_2 gas.

The oxygen or other gases formed at the anode surface can accelerate material loss by 1) channeling of electric current resulting in increased current density, 2) increasing the oxygen chemical potential, 3) removal of reaction products and movement of unreacted slag to surface, and 4) mechanical erosion.

Cation migration from anode results in a cation depletion zone in the slag at the anode surface and decreases the electrical conductivity as indicated by the 3-fold increase in electric potential in the slag at the anode. This may have increased the potential for slag or anode decomposition.

Cation buildup in the slag near the cathode surface increases the charge buildup. Electrochemical reactions probably involve the reduction in oxygen activity resulting in the reduction of other slag species, i.e., iron. Potassium and calcium rich silicates were found in the cathode slag but not at the anode. These potassium rich slags also interact with the cathode grain boundaries (which are nominally high in silica) and ultimate loss in grain integrity.

Certain rare earths in hafnia appear to be more reactive in the electrochemical molten coal slag environmental than others. In MR-1 coal slag, preliminary results suggest that the reactivity of Eu>Sm>Yb>Pr>Y>Tb. In addition, the fluorite structures appear to be more resistant to electrochemical corrosion than the pyrochlore structures. The rare earths tend to be more electrochemically reactive than the hafnium in both molten slag and alkali salts. The terbia-hafnia composition appears to be the most stable.

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