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ELECTROCHEMICAL CORROSION OF LANTHANUM CHROMITE AND YTTRIUM CHROMITE IN COAL SLAG

D. D. Marchant and J. L. Bates

Pacific Northwest Laboratory
Richland, Washington 99352

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INTRODUCTION

Lanthanum chromites have long been considered as electrodes for magnetohydrodynamic (MHD) generator channels (1,2,3,4). These chromites, when doped with divalent ions such as Ca, Mg or Sr, have adequate electronic and electrical conductivity (2), and melting points greater than 2500 K. However, above ~1850 K, selective vapor loss of chromium results in the formation of a La_2O_3 phase (2). The La_2O_3 is hydroscopic at room temperature, resulting in a large volume change and loss of mechanical integrity when exposed to H_2O.

The analogous yttrium chromites have thermal and electrical properties similar to that for the lanthanum chromites (5). Although vapor loss of Cr results in the formation of Y_2O_3, this oxide does not hydrate (5). Corrosion studies (5,6) of yttrium chromite compositions show that doped $YCrO_3$ may be a viable MHD electrode. This paper describes an electrochemical corrosion study of both magnesium-doped lanthanum and yttrium chromites in synthetic coal slag electrolytes. The paper emphasizes possible chemical and electrochemical degradation phenomena, as well as the relative rates of corrosion.

EXPERIMENTAL PROCEDURES

Yttrium and lanthanum chromites were nominally doped with 5 mol% MgO to increase the electrical conductivity. The chromites

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MGW

were fabricated into bars by sintering(a) at high temperature in oxygen partial pressure ranging from 10^{-10} to 10^{-14} atmospheres. The sintered lanthanum chromites were ~91% TD with irregular shaped pores (~3 μm) located at the grain boundaries. The yttrium chromites were ~95% TD with more uniform shaped pores (~1 μm) at the grain boundaries. The lanthanum chromite contained in the grains a uniformly dispersed second phase consisting of magnesium-chromium oxide that had nearly equal amounts of magnesium and chromium. A similar second phase in the grains of the yttrium chromite was magnesium oxide containing Cr (~5 atom%). The matrix grains in both chromites had less than 0.1 wt% magnesium.

Two synthetic slag compositions were used as electrolytes: (1) Montana Rosebud (MR-1) slag contained (in wt%) 42.4 SiO_2, 18.8 Al_2O_3, 13.4 K_2O, 12.9 CaO, 6.9 Fe_2O_3, 4.1 MgO, 0.7 TiO_2, 0.4 Na_2O and 0.2 P_2O_5; and (2) Illinois No. 6 (Ill-6-1) slag contained (in wt%) 39.5 SiO_2, 24.3 Fe_2O_3, 18.4 Al_2O_3, 11.7 K_2O, 5.1 CaO, 1.6 MgO, 1.0 P_2O_5, 0.8 TiO_2, and 0.5 Na_2O. Both slags contained high amounts of potassium to better represent the slags expected in a potassium-seeded MHD generator. The slags were prepared by mixing the oxides or carbonates of the slag constituents (carbonates of calcium, potassium and sodium) and ball milling for 3 h. The powder mixture was calcined in air at 1275 K for 15 min, then melted and homogenized between 1675 K and 1823 K for 16 h in a high purity αAl_2O_3 crucible.

The electrochemical corrosion tests consisted of partially immersing a chromite anode and cathode into molten coal slag, Figure 1, and passing a direct electric current between these electrodes through the coal slag. A constant current was maintained by varying the electric potential. An alumina sleeve surrounded each electrode to channel the electric current through the electrode end. A platinum probe was positioned equidistant from the anode and the cathode to measure the electric potentials of the electrodes. The test was continued for a predetermined time, or until the system resistance exceeded the current/voltage limits of the power supply. The chemical corrosion tests were similar to the electrochemical tests, except electric current was not present.

In all tests, the samples were cooled in the slag to room temperature, mounted in epoxy resin and sectioned parallel to one side of the sample for optical measurements and metallographic examination. The corrosion rates were determined by geometric measurements of the polished cross section and extrapolation to volumetric

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(a) $YCrO_3$ from TransTech Inc., Gaithersburg, MD.
$LaCrO_3$ from Westinghouse Research Center, Pittsburgh, PA.

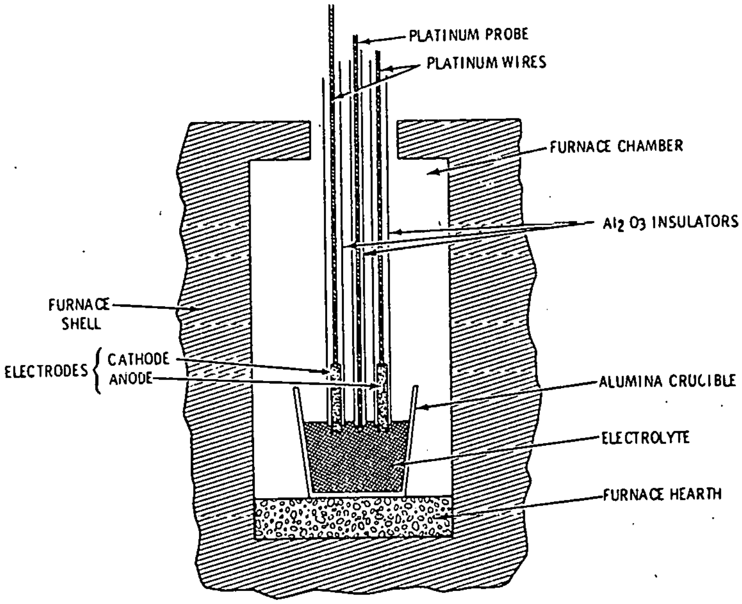

FIGURE 1. Electrochemical Test Configuration

changes. Loss from the interior of the sample, e.g., grain boundaries, was not included in the corrosion rate measurements. A scanning electron microscope equipped with energy-dispersive x-ray analysis (SEM-EDX) was used to identify the microstructural phases and their distribution. The SEM-EDX was quantified using both oxide and metallic standards for elements above an atomic number of 10. The relative accuracy was >10%, and the detection limit was ±0.1 wt%. The quantitative data is expressed as the major elemental components of each phase and the relative atomic ratio of these elements. Unless otherwise stated, the compounds are assumed to be oxides. Although some minor elements may be present, only the major elements are stated in the nominal compound description.

RESULTS AND DISCUSSION

The electrochemical and chemical corrosion tests are listed in Table 1. The electrochemical corrosion rates are also expressed as g/cm^2-h so they can be compared directly with the chemical corrosion rates of the control sample.

Effects Common to Both Chromites

The electrochemical corrosion rates of both the anodes and cathodes in all but one test were at least an order of magnitude

TABLE 1. Summary of Chromite Electrochemical Tests

	Temp, K	Time, ks(h)	coulombs	Anode,* µg/coul	Cathode,* µg/coul	Anode,* g/cm^2-h	Cathode,* g/cm^2-h	Control, g/cm^2-h
Montana Rosebud + 10 mol % K_2O (MR-1)								
$YCrO_3$ + 5 mol % MgO	1733	96.1 (26.7)	8891	13	44	0.04	0.2	--
	1723	86.4 (24.0)	0	0	0	0	0	0.001- 0.003
$LaCrO_3$ + 5 mol % MgO	1723	49.5 (13.8)	3536	131	163	0.6	0.5	--
	1723	86.4 (24.0)	0	0	0	0	0	0.006 - 0.008
Illinois No.6 + 10 mol % K_2O (Il1-6-1)								
$YCrO_3$ + 5 mol % MgO	1729	173.2 (48.1)	15999	11	1	0.04	0.004	--
	1723	86.4 (24.0)	0	0	0	0	0	0.001 - 0.003
$LaCrO_3$ + 5 mol % K_2O	1725	199.8 (55.5)	14185	37	42-120	0.1	0.1-0.3	--
	1723	32.4(9) 0	0	0	0	0	0	0.003 - 0.005

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* current density was 1 amp/cm^2

greater than the chemical corrosion rates. The electrochemical corrosion rates in the MR-1 slag were greater than in the Ill-6-1 slag. Generally, cathode corrosion rates were greater than anode corrosion rates.

The lanthanum chromites had a greater electrochemical and chemical corrosion rate than the yttrium chromites. This greater corrosion rate was consistent with other experimental data (5) which show the lanthanum chromite to degrade even when stored in dry air containing a silica gel dessicant. The degradation appeared to result both from the hydration of lanthanum oxide and of the potassium which had penetrated along the grain boundaries during the test. Hydration was greater on the cathodes than on the anodes. The yttrium chromites exhibited no post test degradation even when exposed to ambient air for several weeks, except in areas where the potassium had concentrated.

Several processes may occur during the passage of direct electrical current to cause the increased electrochemical corrosion over chemical corrosion. At the anode/slag interface, gas bubbles containing O_2 are formed probably from the anodic oxidation of the silicate ions (7), i.e., $SiO_4^{--} \rightarrow SiO_2 + O_2 + 4e^-$. The generation of the bubbles (cavitation) and the movement of the bubbles (sweeping away corrosion products and bringing fresh slag to the reaction interface) can lead to increased corrosion/erosion. More bubbles were generated in the MR-1 slag than in the Ill-6-1 slag at the same current densities.

The bubbles on the anode surfaces were electrically insulating, causing higher localized current densities, higher voltages, and possible higher corrosion rates in adjacent surfaces free of bubbles. The formation and migration of bubbles created electric potential instabilities at the anode. The instabilities in the MR-1 slag were as high as ±50% of the average electric potential, whereas the instabilities in the Ill-6-1 slag were <±10%. These instabilities were not found at the cathode.

The higher iron concentration in the Ill-6-1 slag resulted in a higher electronically conducting slag with higher electrical conductivity. The higher electronic conductivity of the slag reduced the amount of bubbles generated when current was transferred between the electronic-conducting anode and the slag because of reduced ion transport.

Depletion of Ca-, K-, and Fe cations also occurred in the slag adjacent to the anode surface, and these cations tended to concentrate at the cathode. The higher electronically-conducting slag exhibited less cation depletion and concentration.

In all tests, the average electric potential between the anode and cathode increased with time and was greatest at the anode and in MR-1 slag. The formation of reaction products and the depletion of cations may have accounted for most of the electric potential increase.

Chemical Corrosion

Chemical corrosion in the Ill-6-1 slag occurred primarily at the immediate chromite/slag interface. An oxide reaction layer containing Fe, Cr, Al and Mg (atom ratios ~50:17:20:13) was found at this interface. The slag at the interface contained small amounts of La or Y. The grain boundaries at the reaction interface contained slag and La or Y. Slag grain boundary penetration and reaction were greater in the lanthanum chromite and contributed to the higher corrosion rate. A slag-soluble lanthanum silicate was formed along the grain boundaries. In yttrium chromite, the yttrium silicate did not form along the grain boundaries in the interior of the sample, although the boundaries at the immediate chromite/slag boundary contained up to ~50 at % Y. Apparently, the Y was dissolved in the slag with the Cr reacting to form the reaction product.

The chemical corrosion in the MR-1 slag also occurred at the chromite/slag interface with the formation of an oxide reaction product containing Fe, Cr, Al, and Mg (atom ratios 12:36:18:34). The lower Fe in this reaction product was probably due to the lower Fe content in the MR-1 slag. Slag penetration in the grain boundaries was significantly greater in the lanthanum chromite, with lanthanum silicate along the grain boundaries throughout the sample. In both chromites, Ca or K did not concentrate along the grain boundaries, in the reaction product, or in the slag. Yttrium silicate was generally found along the grain boundaries near the bulk slag interface.

Electrochemical Corrosion

In the electrochemical corrosion tests, corrosion of the anodes differed from that of the cathodes. Each will be discussed separately.

Cathodes The degradation of the lanthanum chromite cathodes was significantly more severe in both coal slags than the yttrium chromite cathodes. Although no surface reaction layer was formed, the reaction products at the grain boundaries consisted of La, Al oxides and K, Al oxide phases in the low iron MR-1 slag and Fe, Cr, Al oxides containing some La in the high iron Ill-6-1 slag. No La silicates were formed with the MR-1 slag but La, Ca, Al oxide was formed at the grain boundaries in the sample interior. In Ill-6-1 slags, lanthanum silicates rich in Al, Ca and K were found along the grain boundaries deep inside the sample but not at the slag interface.

Yttrium chromite cathodes in MR-1 slag had a diffuse reaction interface with considerable slag penetration along the grain boundaries, which resulted in grain boundary separation at the slag interface. No identifiable reaction compound was found. Yttrium silicate was found in the interior of the sample along the grain boundaries.

In the I11-6-1 slag, the yttrium chromite cathode had a distinct reaction zone at the slag interface. Significantly less grain boundary penetration and interaction with slag occurred when compared to MR-1. The main degradation appeared to be the dissolution of the grains. Two reaction products were formed at the reaction interface: 1) an yttrium silicate which dissolved in the slag and 2) an oxide containing Fe, Cr, and Al (atom ratios 29:44:27) which coated the cathode.

Anodes. The lanthanum chromite anode formed a distinct reaction layer in the MR-1 slag. This layer was composed of a Cr, Al oxide (atom ratio ~78:22) and a silicate containing La, Al, and Si (atom ratios ~37:14:49). The slag had penetrated the grain boundaries throughout the sample with the La silicate forming in the slag. A crystalline Cr, Mg oxide (atom ratios ~58:42) formed next to the lanthanum chromite grains.

The reaction of the lanthanum chromite with the I11-6-1 slag was also extensive and the reactions were similar to that in the MR-1 slag. The La, Al, and Si silicate (atom ratios ~16:52:32) and Cr, Al oxide (atom ratio ~64:36) were present but with different atom ratios. In addition, an Fe, Al oxide (atom ratio ~19:81) phase was also present.

The yttrium chromite anode in the MR-1 slag formed a distinct reaction layer at the anode surface. This layer was an oxide containing Cr, Al and Fe (atom ratios 69:25:6) with the Y dissolved in the slag.

The reaction of the yttrium chromite anode in the I11-6-1 slag was significantly less than the lanthanum chromite and formed a diffuse reaction layer. Slag had penetrated the grain boundaries and reacted, forming an yttrium silicate and a granular oxide of Fe, Cr and Al (atom ratios ~22:64:14). The yttrium silicate dissolved in the slag, leaving the oxide containing Fe, Cr and Al (atom ratios 33:41:26) on the slag/anode interface. Grain boundary penetration and reaction with the slag was less in the I11-6-1 slag than in the MR-1 slag.

CONCLUSIONS

- Yttrium chromite with 5 mol% MgO exhibits a greater resistance to chemical and electrochemical corrosion than the analogous lanthanum chromite in molten coal slags. Thus, yttrium chromite could be better MHD electrode than lanthanum chromite.

- The chemical and electrochemical corrosion of the chromites is less in the high iron Ill-6-1 slag than in the MR-1 slag. The reduced corrosion is partially attributed to the higher electrical conductivity and higher electronic conductivity of the high iron slag.
- The electrochemical corrosion rates are 10 to 1000 times greater than chemical corrosion rates.
- In general, Y or La in the chromite reacts with slag forming a (La or Y) silicate which is dissolved in the slag. The Cr and Mg remaining in the chromite then reacts with the Al, Fe and Mg in the slag forming a crystalline (Fe, Cr, Al, Mg) oxide with varying cation ratios depending on location in the sample and whether the sample is anode, cathode or control.
- The reactions of the control are closer to those at the anode than those at the cathode. This is attributed to the oxidizing conditions present at the anode.

REFERENCES

1. J. B. Heywood and G. J. Womack, Open-Cycle MHD Power Generation, Pergamon Press, pp 568-570, 609-610, 613 (1969).

2. S. J. Schneider, H. P. R. Frederikse, G. P. Telegin and A. I. Romanov, "Materials," in Open-Cycle Magnetohydrodynamic Electrical Power Generation, M. Petrick and B. Ya. Shumyatsky (eds.), Argonne National Laboratory, Argonne, Illinois, pp 586-589 (1978).

3. Westinghouse Electric Corporation, "Final Report on the Joint U.S.-U.S.S.R. Test of the U.S. MHD Electrode System in the U-0_2 Facility--Phase III," FE-2248-23, Westinghouse Electric, (1979).

4. J. Dong-laing, M. Zhi-giang, J. Wen-hao, W. Da-qian and P. Zhen-su, "A Composite Electrode Material Study and Its Performance in a MHD Test Unit," in Seventh International Conference on MHD Electrical Power Generation, Massachusetts Institute of Technology, Cambridge, Massachusetts, June 16-20, 1980, pp 292-299 (1980).

5. D. D. Marchant and J. L. Bates. "Development of Electrodes Based on Yttrium Chromites and Rare Earth Doped Hafnia for MHD Generator Applications," in 18th Symposium Engineering Aspects of Magnetohydrodynamics, June 18-20, 1979, Butte, Montana, pp D-1.5.1 - D-1.5.8 (1979).

6. A. Drozniak and A. Kozlik-kutak. "Yttrium Chromite $YCrO_3$ as a Material for Electrodes of the MHD Generator," Ibid, pp 300-305 (1979).

7. M. T. Simnad, G. Derge and I. George. "Ionic Nature of Liquid Ion - Silicate Slag," in J. of Metals, Dec:386-1390 (1954).