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HIGH TEMPERATURE ELECTRICAL AND
THERMOPHYSICAL PROPERTIES OF
CERAMIC MATERIALS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This investigation centered on three topics: (1) techniques to determine the electrical conductivity of insulators above 1500 degrees centigrade; (2) charge transport in Ceria-Zirconia solid solutions; and (3) vaporization kinetics of strontium doped lanthanum chromite. Interest in the latter two materials was related to their potential use as high temperature electrodes for magneto-hydrodynamic generators. The major accomplishments are summarized.		

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PREFACE

This report is based on research conducted between September 1971 and July 1973 at the Metallurgy and Ceramics Research Laboratory, Aerospace Research Laboratories, Wright-Patterson AFB, Ohio. The Principal Investigator was Dr. James M. Wimmer with participation by Major L. L. Fehrenbacher. The effort has been documented under Project 7021, "Structure and Properties of Solids," In-house Work Unit 34, "High Temperature Electrical and Thermophysical Properties of Ceramic Materials," and this document constitutes the final report for Work Unit 7021-02-34.

SECTION I .

INTRODUCTION

The objective of this work unit was the determination and study of various factors which define the usefulness of a ceramic material as an insulator, conductor, or semi-conductor in severe thermal environments. If the refractory nature of ceramic materials is ever to be used to full advantage in applications, such as electrodes and insulators in magnetohydrodynamic (MHD) generators, then their high temperature behavior must be defined and understood.

1. HIGH TEMPERATURE ELECTRICAL CONDUCTIVITY MEASUREMENTS

One of the problems encountered in high temperature electrical conductivity measurements, especially in insulators, is extraneous current leakage paths. Surface current paths can generally be eliminated by three-terminal guarding techniques but at very high temperatures a problem often referred to as "gas phase conduction" is encountered. Its source is not well understood but an attempt was made to eliminate it by various shielding methods using single crystal Al_2O_3 as the measured material.

All measurements were performed in air to a temperature of 1750°C . A three probe technique at 10 k Hz was employed, using platinum paste for the electrodes. Many measurements were made of the conductance of the air gap between electrodes (no specimen) as a function of gap geometry and temperature. A rough measurement of the thermionic current between the electrodes and enclosure walls of the sample holder were made and included the effect of a d. c. bias voltage. Some of the conclusions from these experiments follow.

The specimen region as well as the measuring wires must be well shielded with platinum metal foils or coating which are tied to a common ground. The direct measurement of an effective system work function and the experiments using a d. c. bias voltage were consistent and indicated electron transport from the platinum electrodes to the shielded alumina enclosure wall and positive ions from the wall to the electrodes. The work function obtained was between that of alumina and platinum. The leakage or thermionic current between the electrodes and the walls was orders of magnitude less than the thermionic current between the electrodes and the conductivity of single or polycrystalline alumina was several orders of magnitude higher than that of the air gap. Hence, it appears that thermionic emission does not cause serious difficulties up to 1750°C if the proper precautions are taken.

2. CHARGE TRANSPORT IN CERIA-ZIRCONIA SOLID SOLUTIONS

Although zirconia based ceramics are very refractory, the use of stabilized zirconia as an MHD electrode is limited due to both electrolysis and current channeling. The former is due to the high ionic conductivity of the material while the latter is due to the exponential dependence of the electrical conductivity on temperature. The addition of CeO_2 to ZrO_2 results in a predominance of electronic conduction due to the variable valence on the Ce ions. However, below 10^{-6} atm oxygen pressure Ce^{3+} predominates and the structure changes from a tetragonal solid solution to pyrochlore, $\text{Ce}_2\text{Zr}_2\text{O}_7$ and free ZrO_2 and these crystal structure changes result in structural degradation.

Small amounts of Y_2O_3 were added to try to improve the crystal structure stability without seriously impairing the electronic conductivity. Both CeO_2 rich and ZrO_2 rich base compositions were used. The composition 75 m/o ZrO_2 -22m/o CeO_2 -3 m/o Y_2O_3 exhibited the most promise as a high temperature electronic conductor.

3. OXIDATION-VAPORIZATION KINETICS OF LANTHANUM CHROMITE

Lanthanum chromite doped with strontium is a fairly good electronic conductor down to room temperature and has a small activation energy-on the order of a tenth of an eV. This behavior along with a high melting point-about 2500°C for pure LaCrO_3 -makes lanthanum chromite an ideal candidate for high temperature MHD electrodes. The behavior which limits its use however, is the formation and vaporization of CrO_3 at high room temperatures in oxidizing atmospheres. This oxidation-vaporization rate was studied to 1600°C by continuous weighing, using a sensitive microbalance. The loss rate was found to be about two orders of magnitude smaller than that of pure Cr_2O_3 . At 1600°C , $P(\text{O}_2)=0.25$ atm and a flow velocity of 14 cm/sec the loss rate was 1 microgram/cm²/min which converts to a recession rate of about 1mm/yr. The activation energy for the loss rate was 3.6 eV and the rate was essentially independent of Sr content up to 20 m/o Sr.

The ratio of the CrO_3 vapor pressure over LaCrO_3 to that over Cr_2O_3 was calculated by determining the free energy for the reaction $\text{La}_2\text{O}_3 + \text{Cr}_2\text{O}_3 \rightarrow 2 \text{LaCrO}_3$ by a galvanic cell technique. The free energy was found to be given by $\Delta G = 609-8.3T \text{ cal} + 400 \text{ cal}$. At 1900°K the ratio of the CrO_3 vapor pressures was 0.13 which, through the Hertz-Langmuir equation predicts a lower loss rate for LaCrO_3 in agreement with experimental results.

The remaining problems with lanthanum chromite relate to its fabrication. Any excess La_2O_3 will readily hydrate and dense, sintered specimens will completely crumble. In addition, there is a eutectic on both the La_2O_3 and Cr_2O_3 side of the LaCrO_3 compound so that a liquid phase can easily exist at temperatures below the melting point of pure lanthanum chromite. These considerations indicate that compositional control during fabrication is extremely important.

At the culmination of these studies new in-house work units were established which more closely reflect the current research programs of the Metallurgy and Ceramics Research Laboratory. This work unit is therefore being closed-out.