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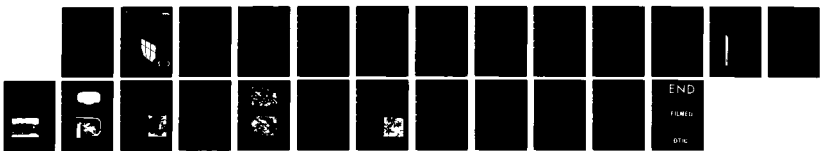
IMPROVED CERAMIC ANODES FOR CORROSION PROTECTION(U)
CONSTRUCTION ENGINEERING RESEARCH LAB (ARMY) CHAMPAIGN
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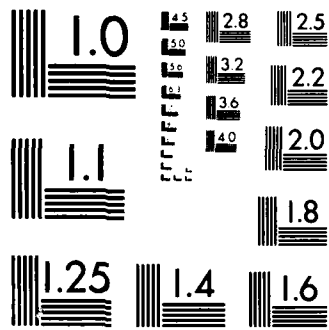
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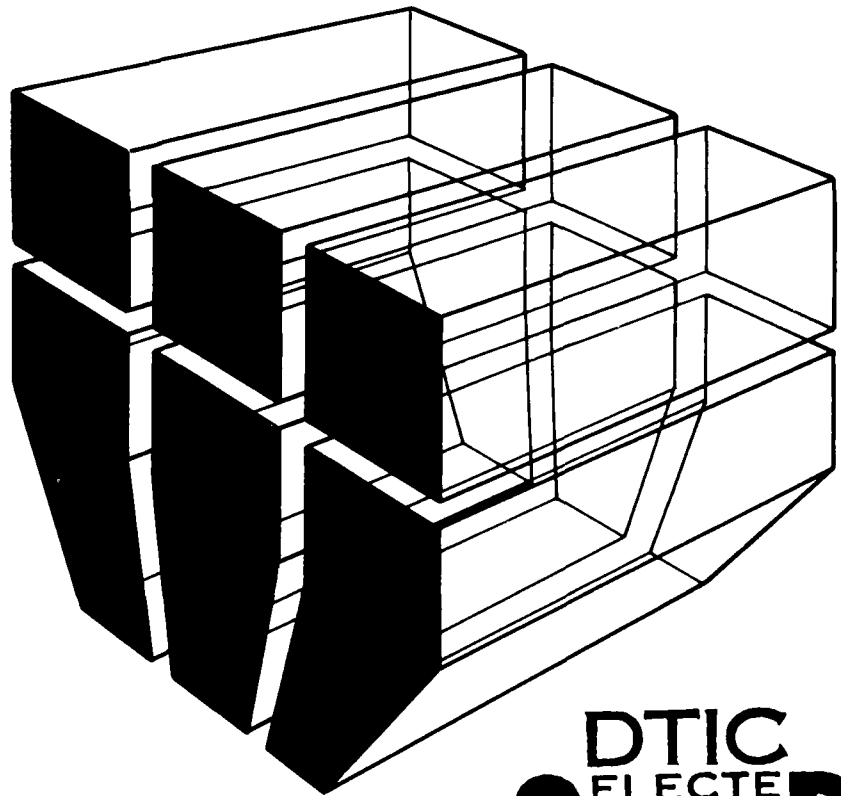


TECHNICAL REPORT M-85/02
November 1984
Corrosion Mitigation in Civil Works Projects

AD-A149 492

IMPROVED CERAMIC ANODES FOR CORROSION PROTECTION

by
J. H. Boy
M. Olson
V. Hock
A. Kumar



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ceramic anodes used for cathodic protection are currently made with expensive metals (niobium, tantalum) as substrates, and these anodes have a limited useful life. This study investigated plasma-sprayed ceramic coatings on aluminum and stainless steel substrates, as well as solid sintered ceramics, as less expensive and longer-lived alternatives. Anodes made of stainless steel substrates with an electroplated coating of a "passive" metal (tantalum) followed by a lithium-ferrite plasma-sprayed coating showed excellent promise. However, a triple layer plasma-sprayed coating system consisting of lithium		

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ferrite over niobium over Ni-Cr-Al-Y sealcoat on 316L stainless steel and aluminum alloy substrates proved unacceptable as a possible anode material because of severe cracking and spalling.

Solid sinter Mn and Mn-Zn ferrites also showed potential. They were fabricated with careful control of the postsintering cooling rate to yield materials with anodic dissolution rates less than 0.5 grams per amp year (g/A-yr). This is considerably improved from the 1 to 2 g/A-yr previously reported for plasma-sprayed lithium ferrite on a valve metal substrate.

Donor doped and reduced solid sintered titanate compounds yielded electrically conductive materials, but they broke down so quickly and severely under anodic polarization testing that they are not suitable for cathodic protection applications.

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FOREWORD

This study was conducted for the Directorate of Civil Works, Office of the Chief of Engineers (OCE), under CWIS 31204 (Corrosion Mitigation in Civil Works Projects). The research was conducted by the Engineering and Materials (EM) Division, U.S. Army Construction Engineering Research Laboratory (USA-CERL). The OCE Technical Monitor was Mr. J. Robertson (DAEN-CWE-E). Dr. R. Quattrone is Chief of EM.

The assistance of Dr. V. A. Amarakoon and Dr. G. P. Wirtz of the Department of Ceramic Engineering, University of Illinois at Urbana-Champaign, is appreciated.

COL Paul J. Theuer is Commander and Director of USA-CERL, and Dr. L. R. Shaffer is Technical Director.



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IMPROVED CERAMIC ANODES FOR CORROSION PROTECTION

1 INTRODUCTION

Background

The U.S. Army Corps of Engineers is responsible for maintaining many types of metallic structures that can corrode, but this corrosion can be stopped by the use of cathodic protection, i.e., by applying a small electric current from an outside source to the corroding structure.

Traditionally, impressed current systems have used anodes that are either inexpensive and very large (high silicon, chromium bearing cast iron), or small and expensive (platinized titanium). Because damage caused by floating debris necessitates relatively frequent replacement of anodes, there is a need for improved cathodic protection systems with affordable anodes that can provide protection with a minimum of installation and maintenance problems.

The use of electronically conducting ceramics as anodes for cathodic protection was investigated by Segan and Kumar.¹ The anodes consisted of a plasma-sprayed lithium ferrite coating on button-shaped titanium or niobium substrates (Figure 1). The dissolution rate of these lithium-ferrite-coated anodes, measured over a 2-month period, was determined to be 1 to 2 grams per amp year (g/A-yr) in an aerated sodium chloride solution.

Drawbacks to these ceramic anodes were high cost due to the niobium substrate and a relatively high dissolution rate due to the ceramic coating. Two steps could be taken to resolve these drawbacks: (1) reduce the cost of the niobium substrate by using niobium-coated steel, (2) increase the life of the ceramic coating by using better ceramic materials.

Objectives

The objectives of this investigation were to develop new plasma-sprayed ceramic anodes to improve performance, minimizing costs by using niobium- or tantalum-coated steel rather than niobium or tantalum

substrates, and to manufacture and test anodes consisting entirely of solid sintered ceramics.

Approach

The state-of-the-art use of electrically conducting ceramic materials for anodes was reviewed. The performances of plasma-sprayed ferrite and other solid sintered ceramics were then evaluated under anodic polarization in various environments to determine the ceramic systems best suited for impressed current anodes.

Mode of Technology Transfer

It is recommended that the information in this report be used to develop procurement specifications for use in the draft Corps of Engineers Guide Specification (CEGS) 2310.

2 COATED ANODES

Plasma-Sprayed Ceramic Coatings

In the previous investigation by Segan and Kumar, the electrically conducting ceramic was plasma-sprayed on two valve metal substrates, titanium and niobium. Valve metals display active-passive behavior in a potentiodynamic scan. In the passive region of the scan, the "passivated" metal forms a surface film which acts as a barrier to corrosion.

Plasma-spraying provides excellent electrical and mechanical ceramic-to-metal interface properties. When the conducting ceramic is sprayed onto a passivated metal, it provides a path of electrical continuity, allowing the anode current to pass easily. If the ceramic coating has interconnected porosity or is damaged, the metal substrate will passivate and protect itself from further corrosion damage. Metal substrates are easier to machine than ceramics, lending themselves to more efficient designs.

A disadvantage of using valve metal substrates is their high cost. Niobium costs up to 18 times more than titanium while tantalum can cost 30 times more. At the time of publication, small quantities of 25.4-mm-diameter niobium rod cost 20 times as much as 316L stainless steel. These metals are also typically harder to machine than most standard engineering metals. For these reasons, it was determined that a thin, nonporous "passivated" metal coating on a more cost-effective metal would provide the best substrate.

¹E. G. Segan and A. Kumar, *Preliminary Investigation of Ceramic Coated Anodes for Cathodic Protection*, Technical Report M-333 ADA133440 (U.S. Army Construction Engineering Research Laboratory [USACERL], August 1983).

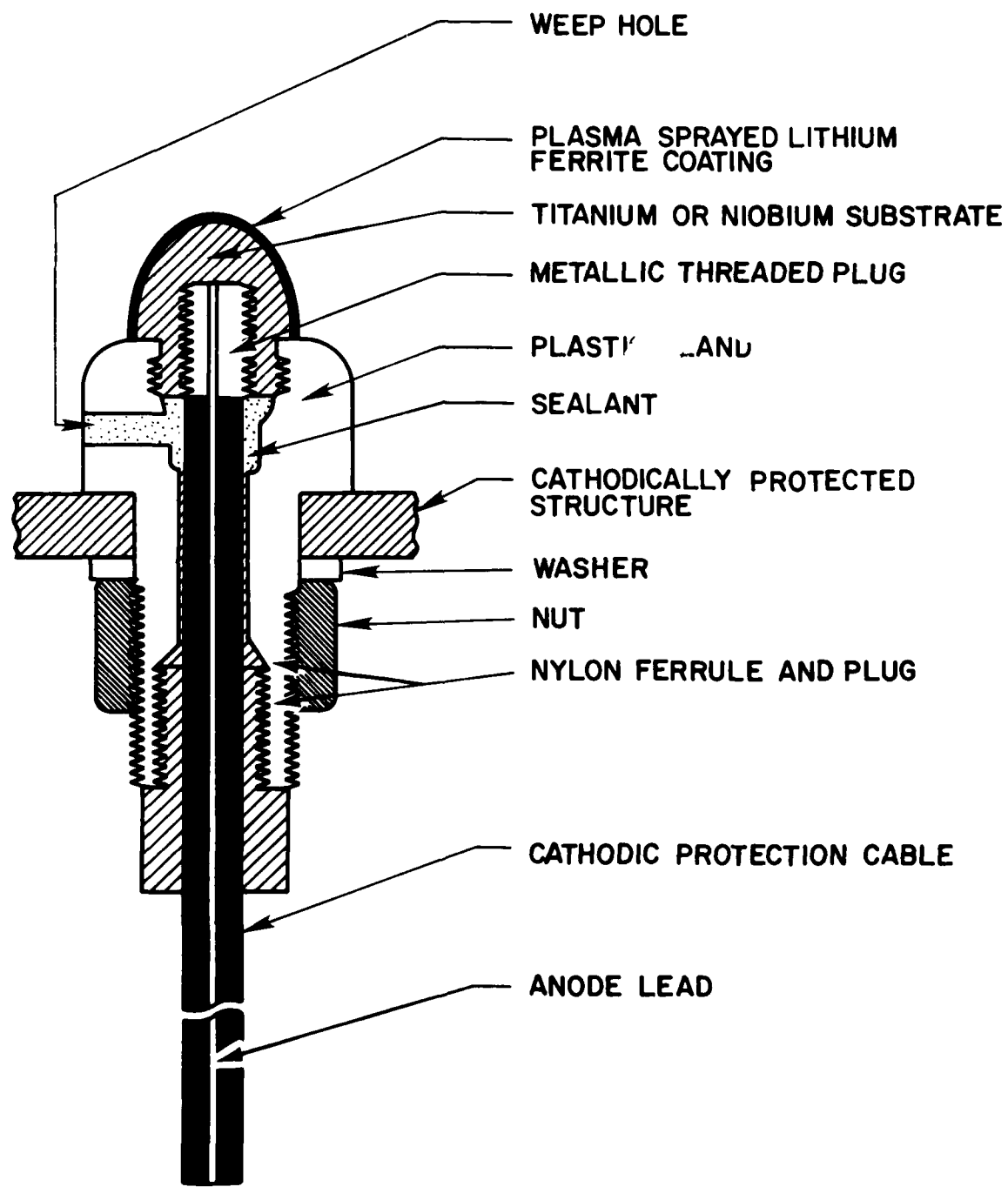


Figure 1. Schematic of plasma-sprayed anode assemblage.

Triple Layer Plasma-Spray System

Because aluminum is lightweight, easily machined, and commonly available, 7075 aluminum alloy was chosen as a potential substrate. A plasma-spray system was used to apply a 0.025 to 0.05-mm nickel-chrome-aluminum-yttrium sealcoat intended to improve the mechanical bond between the aluminum and the passivated metal. This was followed by spraying a 90 percent pure niobium powder to form a 0.5-mm passivated metal coating. The sealed substrates were then sprayed with a 0.5-mm lithium ferrite layer of the composition listed in Table 1. Figure 2 shows a scanning electron micrograph (SEM) of the triply sprayed anode.

Because of the closer match of the coefficients of the metal expansion of the coating to steel than to aluminum, several samples were prepared in a similar manner as above using 316L stainless steel as the base substrate material.

The triple layer plasma-sprayed aluminum and 316L stainless steel anodes were subjected to an anodic polarization test, passing 40 mA of current through the anodes in 3.5 percent NaCl distilled water solution. In all cases, the coating layers displayed severe cracking and spalling (Figure 3). Excessive amounts of corrosion products also were found in solution. These effects may be caused by interconnecting pores in the passivated metal layer which allow contact between the steel or aluminum and the surrounding electrolyte. The resulting corrosion of the metal connection would form metal oxides and other corrosion products. Since these products require more physical space than the pure metal, they force the coating layers to crack and spall.

Electroplated Tantalum and Plasma-Sprayed Lithium Ferrite

A second coating method investigated was electroplating from molten valve metal salts. Again, 316L stainless steel was chosen as the substrate material because of its corrosion resistance. The substrates were polarized in a molten tantalum fluoride salt solution maintained at over 800 C. A 0.125-mm coating was deposited at a rate of 0.35 $\mu\text{m/hr}$ under an argon atmosphere. Some of the plated substrates were then plasma-spray coated with a 0.5-mm conducting lithium ferrite layer.

Both ceramic-coated and uncoated tantalum plated substrates were then subjected to an anodic polarization test by passing 40 mA of current through the anodes in 3.5 percent NaCl in distilled water solution

for 24 hours. Also, a potentiodynamic scan of the tantalum plated coating was taken.

Preliminary investigation of the substrates shows great promise. All samples passed the initial polarization test with very little dissolution evident. The potentiodynamic scan indicated that the electroplated tantalum coating will remain passive at typical anode potentials. Further investigation will determine if the coating retains its high quality under various conditions over long periods of times, such as 6 months.

3 SOLID SINTERED ANODES

Titanate-Based Perovskite Ceramics

Many electrical ceramics have a common crystal structure corresponding to the structure of the mineral perovskite CaTiO_3 . In the ideal form, the unit cell can be represented by calcium at the corner of a cube with a titanium atom at the body-centered position and oxygen atom at the face-centered position. In the generic perovskite structure, ABO_3 , the A cation is coordinated with 12 oxygen atoms and the B cation with six.

The most common perovskite compounds are described by the general formula $\text{A}^{2+}\text{B}^{4+}\text{O}_3$, where the A cations are alkaline earths Ca, Sr, Ba, Mg, Pb, or Cd, and the B cations include Ce, Fe, Sn, Ti, or Zr. The best known are the titanates because of the ferroelectric properties exhibited by the barium and lead compounds.²

Electrical conductivity in perovskite ceramics is determined by the defect chemistry of the sample. The principal defects of interest at dopant ions of a different valency and deviation from the stoichiometric composition. Pure barium titanate is an insulator, with electrical resistivity of about 10^{14} ohm/cm at room temperature. Additions of precisely controlled amounts of dopants make BaTiO_3 a semiconductor, with resistivities of about 10 ohm/cm. Heavily doped samples are insulators. Dopant ions must be of similar size to the ion being replaced, with ionic radius difference of 15 percent or less.³ Dopant cations must also have a

²F. S. Galasso, *Structure, Properties and Preparation of Perovskite-Type Compounds* (Pergamon Press, 1969).

³D. B. Meadowcroft, *Proceedings of the International Conference on Strontium Containing Compounds*, edited by T. J. Grey (1973), pp 119-136.

Table 1

Chemical Analysis of Plasma-Sprayed Lithium Ferrite on Titanium Substrate*

	Weight Percent	Mole Percent
Iron	69.22	40.49
Manganese	3.05	1.81
Lithium**	1.46	6.87
Zinc	1.43	0.72
Magnesium	0.008	1.08×10^{-2}
Calcium	0.27	0.22
Nickel	0.082	0.46
Oxygen (estimated)	24.375	49.77
Other Approximate:		
Titanium	0.02	1.36×10^{-2}
Aluminum	0.01	1.21×10^{-2}
Boron	0.01	3.02×10^{-2}
Silicon	0.005	5.82×10^{-3}
Chromium	0.003	1.88×10^{-3}
Copper	0.003	1.54×10^{-3}
Molybdenum	0.003	1.02×10^{-3}
Cobalt	0.001	5.54×10^{-4}
Silver	0.0005	1.51×10^{-4}
Sodium Questionable, If Present	0.05	≈ 0

*Analysis performed by x-ray fluorescence on a fused sample of plasma-sprayed lithium ferrite.

**Lithium analysis performed by atomic absorption.

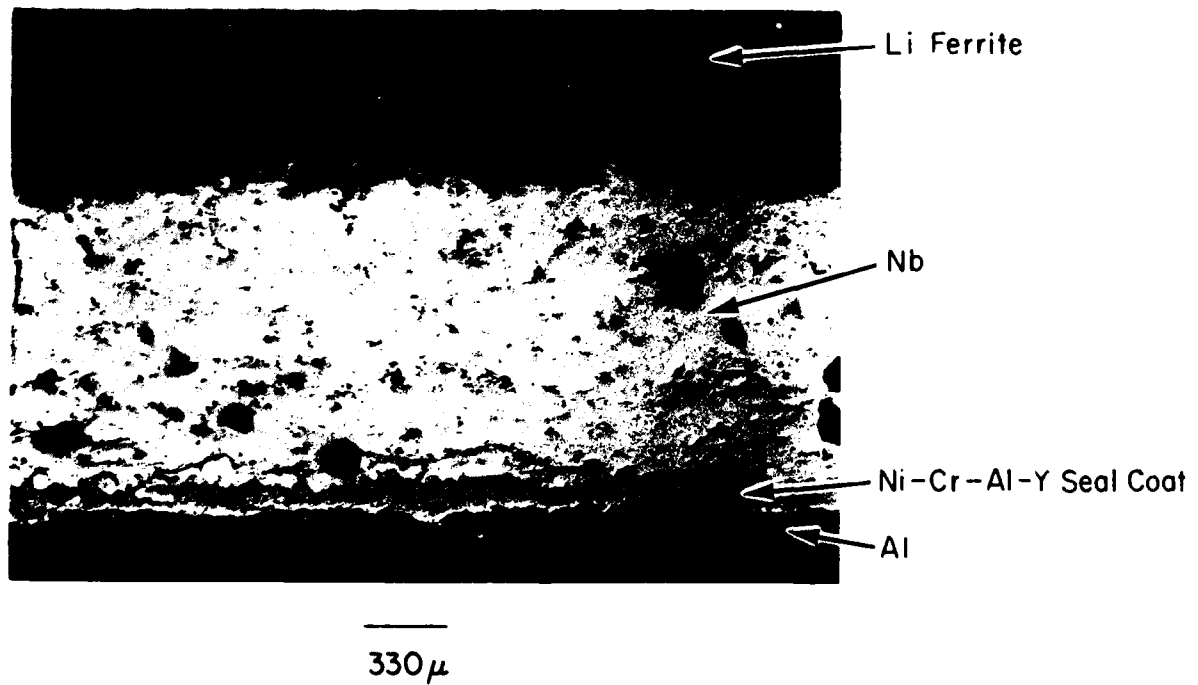


Figure 2. Cross section of triple layer plasma-sprayed anode.



3a

—
25.4 mm



3b

—
6.35 mm

Figure 3. Triple layer plasma-sprayed anode following anodic polarization testing.

different valence from the ion being replaced, with higher valence to yield n type semiconductors. Dopants can be substituted either on the A site (e.g., Lanthanides, Sb^{3+} , Bi^{3+} , and Y^{3+}) or at the B site (e.g., Nb^{5+} , Ta^{5+} , V^{5+} , Sb^{5+} , and W^{6+}).⁴ To enhance perovskite conductivity, one can simultaneously donor dope both the A and B sites—for example La^{3+} and Nb^{5+} , respectively—in $SrTiO_3$.

Oxygen vacancies in the perovskite crystal structure formed during high temperature processing in a reducing (N_2) atmosphere can be quenched in at room temperature, with the compensating electrons remaining available for conduction. Thus, undoped $BaTiO_3$ can be made semiconducting by sintering in a reducing atmosphere, although both chemical doping and reduction are typically combined.⁵ For $SrTiO_3$, chemical doping with tungsten was not sufficient to produce semiconducting samples; the samples also required sintering in a reducing atmosphere to yield resistivities in the range 10 to 10^2 ohm cm.⁶

Titanate samples were prepared using typical ceramic processing techniques. Commercially available electronic grade titanate powders and reagent grade oxide additives were used. The starting materials were weighed to yield the desired composition, and ball milled in an alcohol/water solution for 8 hours. A 0.5 wt percent of SiO_2 and 0.5 wt percent of $CaCO_3$ were added to each batch to enhance the densification by the formation of a liquid phase. A polyvinyl alcohol solution was added during the last hour of milling to enhance the pressing of the sample pellets. The slurry was filtered and dried to the desired moisture content, approximately 3 percent. The resulting powder was sieved through a 30 mesh screen, then pressed into 1.55-cm-diameter pellets at 103 MPa. These pellets were subsequently sintered in an atmosphere-controlled furnace. The titanate samples were fired at $1450^\circ C$ for 4 hours. During the heating and the initial 3 hours of sintering, flowing air was used. During the last hour of sintering and during cooling, a reducing atmosphere of 90 percent N_2 and

10 percent H_2 was used. The resulting samples were dark in color, indicating successful reduction.

The samples were tested for density, then electroded with sputtered gold for electrical conductivity testing, followed by encapsulation in epoxy and corrosion testing. The corrosion testing consisted of polarizing the sample with an applied current density of 0.02 A/cm² in a 3.5 percent NaCl aqueous solution. Scanning electron microscopy was used to examine the microstructure of the samples as sintered and after corrosion testing. To observe the sintered microstructure, the samples were prepared using standard metallographic techniques. The samples were then thermally etched at $1425^\circ C$ in a reducing atmosphere to enhance grain boundary relief. The fired microstructure of the $SrTiO_3$ sample shown in Figure 4 is representative of the titanate samples and is typical of a densely sintered ceramic.

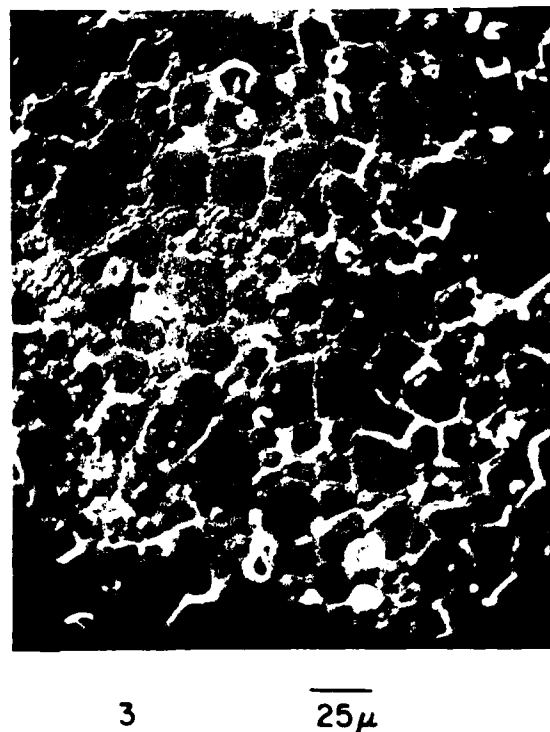


Figure 4. Scanning electron micrograph of sintered $SrTiO_3$ sample before testing.

⁴B. M. Kulwicki, "PTC Materials Technology, 1955-1980," *Grain Boundary Phenomena in Ceramics*, Vol 1, *Advances in Ceramics*, edited by L. M. Levinson (1981), pp 138-154.

⁵H. P. R. Frederikse, et al., "Electronic Transport in $SrTiO_3$," *Physical Review*, Vol 134, No. 2A (1964), pp A442-445.

⁶K. D. Budd and D. A. Payne, "Internal Boundaries in Fine Grain WOP₁ Doped $SrTiO_3$," Presented Amer. Ceramic Society (April 1983).

Table 2 summarizes data obtained for the various titanate compounds. All samples had conductivities below $0.01 \text{ (ohm cm)}^{-1}$. The corrosion test showed that the reduced titanate compounds were typified by severe spalling or flaking of material from the sample face. The time to failure was less than 1 minute. Figure 5 shows an SEM of the sample surface after corrosion testing. The spalling, believed to be due to reoxidation of the surface of the reduced titanate, is indicated in Figure 6, the potential vs time plot obtained during the CaTiO_3 sample polarization testing.

The test consists of applying the necessary potential to drive a constant current through the sample. Initially, the sample was conducting, but in a very short time, the required potential increased rapidly, corresponding to the sample's loss of conductivity. This is believed to be caused by the formation of an insulating surface layer. As this surface layer flaked off, new conducting surface was exposed.

Selective donor doped and reduced titanate compounds were fabricated and yielded electrically conducting material. However, these compounds were found unsuitable as potential anode material for cathodic protection systems because of their rapid spalling and flaking.

Ferrites

The largest group of ferromagnetic oxide compounds are the ferrites of iron having the spinel structure and the general formula AB_2O_4 . There are two idealized structures in the spinel family. In the "normal" spinel, all the divalent ions are on the tetrahedral (A) site, e.g., $(\text{Zn}^{2+})(\text{Fe}^{3+})_2\text{O}_4$. In the "inverse" spinel, half of the trivalent ions occupy the A site, while the remaining trivalent and the divalent ions are distributed on the B site, e.g., $(\text{Fe}^{3+})(\text{Fe}^{2+}, \text{Fe}^{3+})_2\text{O}_4$.

Electrical conductivity in ferrites has been described by a "hopping" mechanism, in which charge carriers

"jump" or "hop" from one ionic site to the next. This will occur if ions of the same element, but different valency are present on the same crystallographically equivalent lattice site; e.g., Fe^{2+} and Fe^{3+} or Mn^{2+} and Mn^{3+} are both present on the B site of the spinel structure. Electrical conduction will occur by an electron "hopping" from an Fe^{2+} to an Fe^{3+} ion. By repeating this process throughout a lattice, electrons can move through the material under a net electrical field. The resulting conductivity of a material will be determined by the cation distribution, which is dependent on the composition, processing, and microstructure.⁷

Mn-Zn ferrite was determined to be an 80 percent normal spinel, with 80 percent of the Mn^{2+} on the normal or A site and 20 percent on the inverse B site.⁸ An investigation⁹ of the postsintering thermal processing of Mn-Zn ferrites found that the time to cool the sample from sintering temperature to room temperature significantly affected the electrical conductivity. Samples were prepared from reagent grade oxide chemicals, using standard ceramic processing techniques. The samples were sintered in an atmosphere-controlled furnace at 1250°C according to the temperature-time-atmosphere profile given in Figure 7.

The compositions investigated are summarized in Table 3, which shows the electrical resistivities and densities of the Mn-Zn ferrites. All Mn-Zn ferrites compositions quenched after sintering had resistivities about 2 to 4 orders of magnitude higher than the

⁷K. S. Stanley, *Oxide Magnetic Materials* (Clarendon Press, 1972).

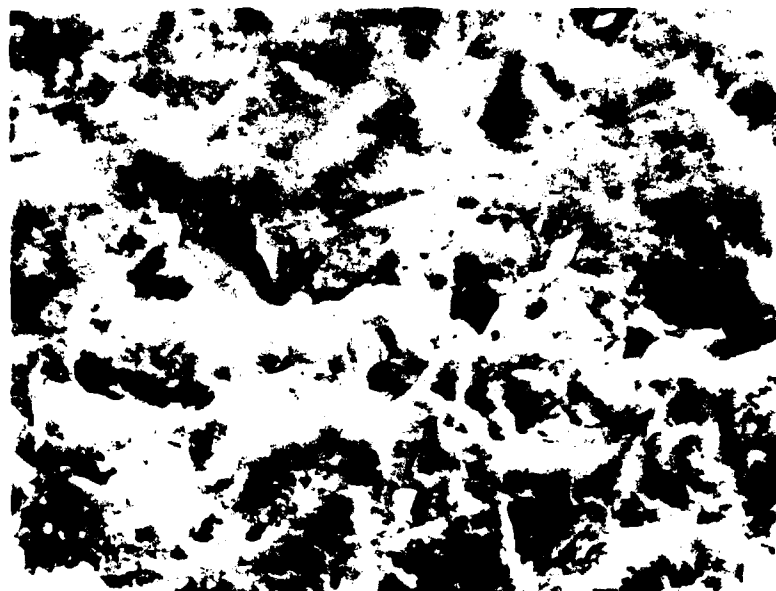
⁸J. M. Hastings and L. M. Croliss, *Physics Review*, Vol 104, No. 2 (1956), p 328.

⁹V. R. W. Amarakoon, G. P. Wirtz, D. A. Payne, B. V. Raju, and J. H. Boy, "The Effect of Post Sintering Treatment on Electrical Properties of Mn-Zn Ferrites," Presented to the Amer. Ceramic Society, Pittsburgh, PA (May 1984).

Table 2

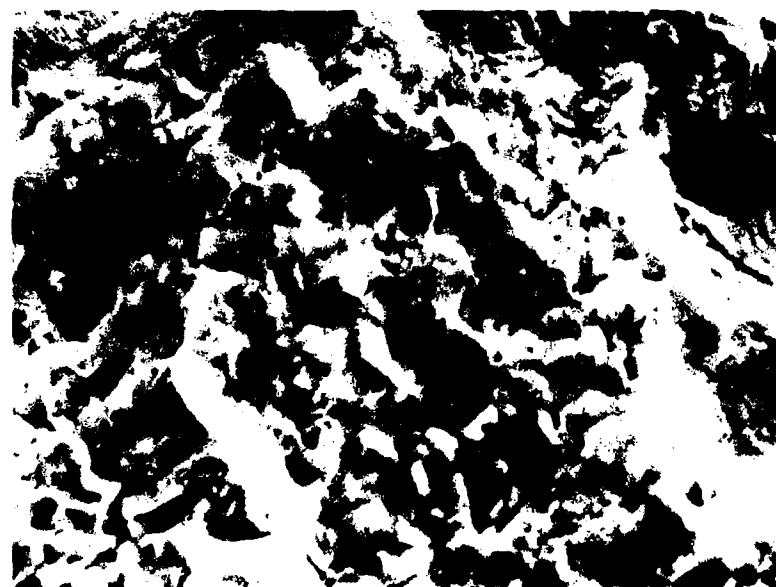
Properties of Titanate Compounds as Possible Anodes

Material	Oxide Dopant	Density Percent Th	Resistivity ohm/cm	Corrosion Testing
BaTiO_3	La, W	94	6×10	severe spalling
SrTiO_3	La, W	99	5×10	severe spalling
CaTiO_3	La, W	98	1×10^2	sample stopped conducting
TiO_2	Nb	93	< 1	severe spalling



10 μ

a.



10 μ

b.

Figure 5. Scanning electron micrograph of titanate samples after anodic polarization testing: (a) SrTiO_3 ; (b) BaTiO_3 .

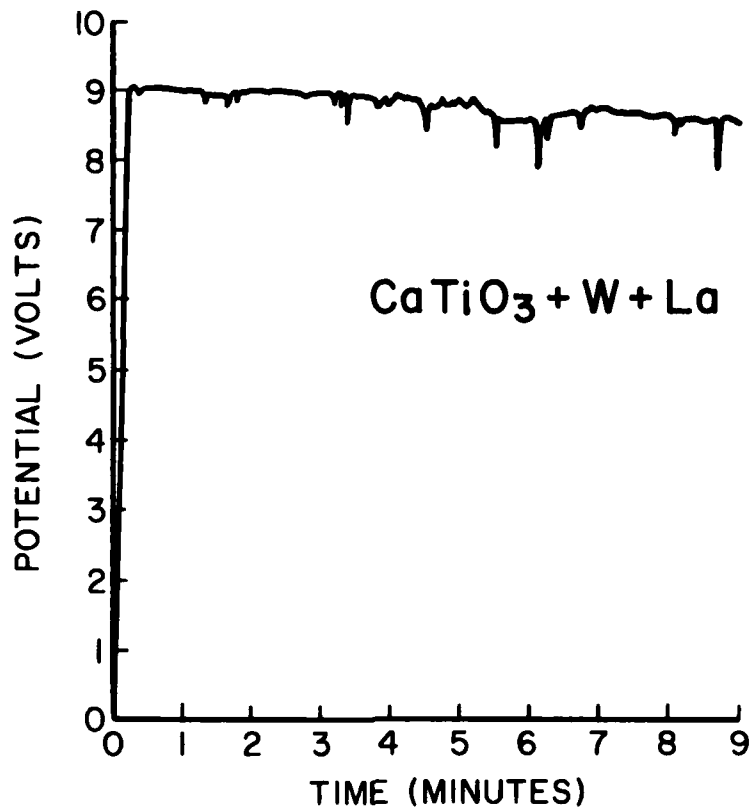


Figure 6. Potentiodynamic scan of CaTiO_3 sample.

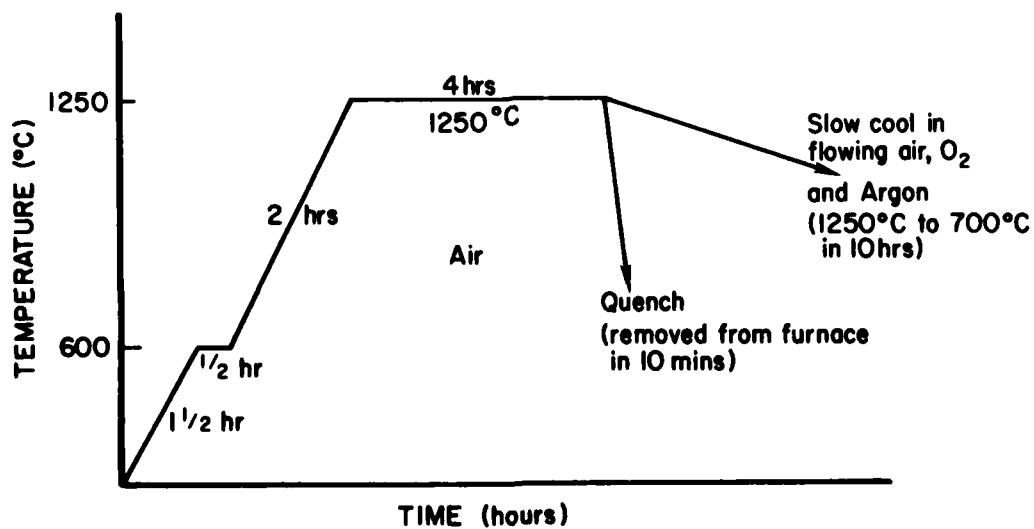


Figure 7. Heating schedule for ferrite samples.

Table 3

**Electrical Resistivity and Density of Mn-Zn Ferrites
as a Function of Postsintering Cooling Treatments**

$Mn_{1-x}Zn_xFe_2O_4$ (x)	Postsintering Treatments	Resistivity (Ohm/cm)	Density (Percent Th)
0.00	Quenched	$4.0 \cdot 10^4$	92.0
	slowly cooled in air (10 hr)	$\bar{1} \ 2$	94.9
0.20	Quenched	$1.3 \cdot 10^4$	92.0
	slowly cooled in air (10 hr)	$\bar{2} \ 3$	95.5
0.45	Quenched	$1.0 \cdot 10^4$	95.4
	slowly cooled in air (10 hr)	$\bar{1} \ 2$	98.5
0.5	Quenched	3 4	95.2

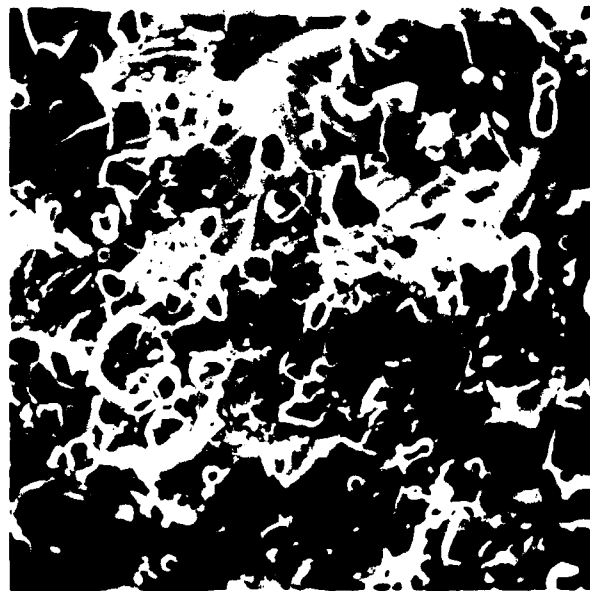
resistivities of the slowly cooled samples. The slowly cooled samples were all conducting (1 to 5 ohm/cm) irrespective of cooling atmosphere. Adding 0.1 wt percent CaO and SiO₂ units improved the densities, but did not significantly affect the resistivities of the quenched or slowly cooled samples. An SEM of a slowly cooled sample is shown in Figure 8.

The significant change in resistivity due to difference in cooling rates was due to a change in the bulk properties of the Mn-Zn ferrites. This was determined by electrical impedance and magnetic Curie point analysis. X-ray diffraction analysis of the slow-cooled samples indicated the formation of an Mn-rich phase. The removal of Mn from MnFe₂O₄ during slow cooling would result in the formation of an Fe rich phase with both Fe²⁺ and Fe³⁺ ions, which would explain the high conductivity.

The dissolution rates of the anodes were determined in the laboratory by immersing the sample material in distilled water containing 3.5 percent NaCl, at various current loadings. The amount of dissolved ions in solution was determined by atomic absorption analysis. The anode dissolution rates (Table 4) were ascertained based on the concentration of the individual ions found in solution and the stoichiometry of the sample.

The anode dissolution rate for the slow-cooled MnFe₂O₄ sample was 0.032 g/A-yr based on Mn, and 0.74 g/A-yr based on Fe with an average rate of 0.38 g/A-yr. The substitution of 20 percent of the Mn by Zn yielded a composition of Mn_{0.8}Zn_{0.2}Fe₂O₄. The anode dissolution rate for slow-cooled samples ranged

from 0.13 to 0.20 g/A-yr based on Mn and between 0.53 to 0.46 g/A-yr based on Fe and averaged 0.33 g/A-yr independent of current density of the test.



28 μ

Figure 8. Scanning electron micrograph of slowly cooled Mn ferrite sample.

Table 4

Dissolution Rates of Sintered Ferrites in 3.5 Percent NaCl Distilled Water Solution

Material	Current Density (A/m ²)	Anode Dissolution Rate (g/A-yr) Based On:			Average Anode Dissolution Rate (g/A-yr)
		Fe	Mn	Zn	
MnFe ₂ O ₄	250	*	*	*	
MnFe ₂ O ₄	1000	0.74	0.03	0.38	
Mn _{0.8} Zn _{0.2} Fe ₂ O ₄	1000	0.46	0.20	0.33	
Mn _{0.8} Zn _{0.2} Fe ₂ O ₄	100	0.53	0.13	0.33	
Mn _{0.5} Zn _{0.5} Fe ₂ O ₄	100	*	*	*	

*Below sensitivity limit of test.

The quenched sample of the same composition spalled severely during testing. The dissolution rate for the Mn_{0.5}Zn_{0.5}Fe₂O₄ sample was below the sensitivity of the analytical test.

The dissolution rates obtained in this study for Mn and Mn-Zn ferrites fired in an ambient atmosphere and subjected to careful control of the post-sintering cooling treatment are superior to those reported by Wakabayashi and Aoki.¹⁰ They recorded Mn-ferrite and Zn-ferrite samples with dissolution rates of 2.7 and 3.2 g/A-yr, respectively—substantially higher than the 0.38 and 0.33 g/A-yr obtained for the Mn-ferrite and 80 percent Mn-20 percent Zn ferrite samples.

4 CONCLUSIONS AND RECOMMENDATIONS

While aluminum and stainless steel are less expensive substrate materials than niobium and titanium, they do not make acceptable anodes when coated with Ni-Cr-Al-Y, then niobium, then lithium ferrite in a triple layer plasma-sprayed system. These samples cracked

¹⁰A. Wakabayashi and T. Aoki, "Characteristics of Ferrite Electrodes," *Journal de Physique*, C1, Vol 38, No. 4 (1977), pp 241-244.

and spalled severely when subjected to anodic polarization testing.

Anodes consisting of a stainless steel substrate with a molten salt electroplated coating of tantalum ("passive" metal) followed by a lithium-ferrite plasma-sprayed coating showed great promise as a potential anode material, with the advantage of a more cost-effective substrate.

Donor doped and reduced solid sintered titanate compounds yielded electrically conducting materials, but they also degraded quickly and severely under polarization testing. These materials are not suitable for cathodic protection anodes.

Solid sintered Mn and Mn-Zn ferrite materials were fabricated with careful control of the postsintering cooling rate to maximize the electrical conductivity. The anodic dissolution rates of Mn and Zn ferrites were less than 0.5 g/A-yr based on the principal elements. This is better than the 1 to 2 g/A-yr reported for previously used plasma-sprayed lithium ferrite.

It is recommended that improved anodes made of niobium-coated stainless steel coated with plasma-sprayed Mn-Zn ferrites be tested in the field to provide a better understanding of ceramic anode behavior. It is also recommended that dissolution mechanisms and the effects of structure and composition on the electrochemical stability of ceramic semiconductors be investigated further.

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